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The Analysis of Permissible Explosives

(Bulletin No. 96. Bureau of Mines)

By C. G. STORM



¶ This Thesis was submitted to the Faculty of the Graduate School of George Washington University in part satisfaction of the requirements for the degree of Doctor of Philosophy.

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May 6, 1916.

To the Faculty of Graduate Studies

Gentlemen:

With this I present the thesis entitled "The Analysis of Permissible Explosives" submitted by Mr. Christian George Storm in part satisfaction of the requirements for the degree of Doctor of Philosophy.

This investigation was undertaken on my suggestion and was carried out directly under my supervision in the laboratory of the U. S. Bureau of Mines at the Pittsburgh Testing Station. Mr. Storm has performed his work with complete thoroughness and he has evinced a broad and complete comprehension of his subject with the result that he has produced an original contribution to knowledge of great value.

I recommend that this thesis be accepted; that Mr. Storm be permitted to defend it before the Board of Experts; and that, provided all other requirements be satisfied, the degree of Doctor of Philosophy be conferred upon him.

Yours very truly

(Signed) CHARLES E. MUNROE

Professor of Chemistry

March 20, 1916.

DR. CHARLES E. MUNROE

Dean, Faculty of Graduate Studies

The George Washington University

Dear Dean Munroe:

I have read with great interest the thesis of Christian George Storm, B.S., 1898., M.S., 1899, Columbian University, dated February, 1916, on the Analysis of Permissible Explosives, submitted to the Faculty of Graduate Studies in part satisfaction of the requirements for the degree of Doctor of Philosophy.

The subject matter of this thesis appeals to me as vitally important from an industrial point of view; I find that the author has presented many distinctly original methods of analysis which together constitute a notable contribution to the literature of Analytical Chemistry; and the comprehensive and masterful treatment of the subject is deserving of the highest recognition.

I therefore take great pleasure in recommending that this thesis be accepted in satisfaction of the requirement, in this particular, for the degree of Doctor of Philosophy.

Very truly yours

(Signed) OTIS D. SWETT

Asst. Professor of Chemistry

Co-referee

This Thesis was publicly defended on May 15, 1916, before a Board of Experts, officially designated by the University to conduct the disputation and report upon the candidate.

Dr. A. L. Kibler, Chief Chemist, Picatinny Arsenal, Dover, N. J., Mr. G. W. Patterson, Powder Expert, U. S. Navy Department, and Dr. Walter O. Snelling, Consulting Chemist, with Dr. Frank Wigglesworth Clarke, Professor of Mineral Chemistry, presiding, composed this Board, which reported as follows:

Washington, D. C., May 15, 1916.

To the President,
George Washington University

Dear Sir:

The undersigned have heard the reading of the thesis of Christian George Storm on "The Analysis of Permissible Explosives," and have personally questioned Mr. Storm in regard to his work, which questions he has successfully and satisfactorily answered.

We feel that he has completed this requirement in a satisfactory manner, and recommend the acceptance of his thesis as part requirement for the degree of Doctor of Philosophy.

(Signed) A. L. KIBLER
G. W. PATTERSON
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Member and Abstractor, American Chemical Society; Secretary, Pittsburgh Section, American Chemical Society.

Author of numerous papers in U. S. Government publications and scientific journals dealing with the properties and analysis of explosives.

Bulletin 96

DEPARTMENT OF THE INTERIOR

FRANKLIN K. LANE, SECRETARY

BUREAU OF MINES

VAN. H. MANNING, DIRECTOR

THE ANALYSIS OF PERMISSIBLE
EXPLOSIVES

BY

C. G. STORM



WASHINGTON
GOVERNMENT PRINTING OFFICE
1916

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First edition. January, 1916.

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THE ANALYSIS OF PERMISSIBLE EXPLOSIVES.

By C. G. STORM.

INTRODUCTION.

Permissible explosives are those that have passed the tests prescribed by the Bureau of Mines for explosives intended for use in coal mines, and are therefore recommended by the bureau as suitable for this class of work when used under the prescribed conditions. The tests for permissible explosives and the conditions prescribed for their use are described in Miners' Circular 6 of the Bureau of Mines.* Up to June 1, 1915, 168 explosives had been classed as permissible explosives; 133 of them were then on the bureau's "permissible list" and 35 had been withdrawn by the manufacturers.

In addition to the required physical tests, each explosive is subjected to a complete chemical examination in order that its exact composition may be known and also that the composition of future samples of the same explosive collected in the field may be compared with that of the sample which originally passed the bureau's tests, for by such comparison it may be possible to ascertain whether or not the explosive as supplied to the miner is still "permissible."

This bulletin is published primarily for the purpose of informing manufacturers of such explosives as to the methods used by the Bureau of Mines in the analysis of samples received for tests to determine their permissibility. Such information may be of value in cases of possible controversy over the results obtained in the analysis of a field sample as compared with those obtained in analyzing the sample originally tested by the bureau. Also, a description of the methods used by the Bureau of Mines in the analysis of explosives should be of assistance to the many chemists engaged in similar analytical work.

ACKNOWLEDGMENTS.

The writer desires to acknowledge the valuable assistance of A. L. Hyde, W. C. Cope, J. H. Hunter, J. E. Crawshaw, and C. A. Taylor, of the explosives chemical laboratory of the Bureau of Mines, in obtaining the analytical results included in this bulletin.

* Hall, Clarence, Permissible explosives tested prior to Jan. 1, 1912, and precautions to be observed in their use: Miners' Circular 6, Bureau of Mines, 1912, 20 pp.

NATURE OF PERMISSIBLE EXPLOSIVES.

In explosives intended for use in open work, such as quarrying, the factor of prime importance is efficiency in bringing down the material to be blasted. Such explosives are therefore so constituted as to produce the desired effects without regard to the temperature of explosion, the amount of flame produced, or the nature of the gaseous products. The properties essential to explosives used in tunneling are efficiency and the absence of poisonous gases in the products of explosion. Coal-mining explosives should possess not only all of these qualities but should evolve on explosion flames of relatively low temperature.

By proper changes in its composition or in the properties of its components, an explosive of any type may be altered so that on explosion it will not ignite an explosive mixture of coal gas or coal dust or both with air.

The general methods in use at the present time for bringing about a reduction in the flame temperature of explosive mixtures have been discussed in another publication of the Bureau of Mines,* and are summarized as follows:

- (a) The addition of an excess of carbon, for the purpose of reducing the amount of carbon dioxide formed.
- (b) The addition of free water.
- (c) The addition of solids holding water of crystallization.
- (d) The addition of inert materials.
- (e) The addition of volatile salts.

The effects of such additions have been considered from the viewpoint of thermochemistry in the publication referred to. This bulletin discusses the variations in the methods of chemical analysis made necessary by such alterations in the composition of the ordinary types of blasting explosives.

CLASSIFICATION OF PERMISSIBLE EXPLOSIVES.

Permissible explosives have been classified, according to their characteristic components, into four general classes^b as follows:

Class 1—Ammonium-nitrate explosives.

Class 2—Hydrated explosives.

Class 3—Organic nitrate (other than nitroglycerin) explosives.

Class 4—Nitroglycerin explosives.

* Hall, Clarence, Snelling, W. O., and Howell, S. P., Investigations of explosives used in coal mines, with a chapter on the natural gas used at Pittsburgh, by G. A. Burrell, and an introduction by C. E. Munroe: Bull. 15, Bureau of Mines, 1912, pp. 51-58.

^b Hall, Clarence, Permissible explosives tested prior to Jan. 1, 1912, and precautions to be taken in their use: Miners' Circular 6, Bureau of Mines, 1912, pp. 12-14; Permissible explosives tested prior to Jan. 1, 1914: Tech. Paper 71, Bureau of Mines, 1914, pp. 8-10.

Of the 168 explosives which passed the bureau's tests for permissibility up to June 1, 1915, 75 were explosives of class 1, 9 were of class 2, 9 were of class 3, and 75 were of class 4. Of the 35 of these which have been withdrawn from the list 14 were of class 1, 3 of class 2, 6 of class 3, and 12 of class 4.

Although, up to June 1, 1915, no explosives containing chlorates or perchlorates as their characteristic ingredients have been placed upon the bureau's permissible list, a number of such explosives have been tested by the bureau. The chlorate or perchlorate explosives form an additional class to the four classes enumerated above, but because they are presented for testing, methods for their analysis are discussed herein.

GENERAL CHARACTERISTICS OF PERMISSIBLE EXPLOSIVES.

AMMONIUM NITRATE EXPLOSIVES.

Ammonium nitrate, although not commonly regarded as an explosive substance, has been shown to be capable of explosive decomposition. Berthelot^a gives seven different decomposition reactions of ammonium nitrate, three of which are explosive in their nature. The maximum effect is produced by the reaction—



which results under the influence of sudden high temperature and pressure, as by the action of a strong detonator. The effect of weaker detonators is to produce other forms of decomposition, yielding oxides of nitrogen.

Lobry de Bruyn^b succeeded in detonating a charge of 180 grams of pure ammonium nitrate compressed in an 8-cm. shell, using a priming charge of 20 to 30 grams of Bellite (a mixture of ammonium nitrate and dinitrobenzene), and a detonator containing 1 gram of mercury fulminate. The shell was disrupted into many fragments. Without the priming charge of Bellite, a detonator containing 3 grams of mercury fulminate produced only incomplete explosion of the ammonium nitrate.

Lheure^c obtained complete detonation of cartridges of pure ammonium nitrate loaded in drill holes in rock, using a detonating fuse (cordeau detonant) of trinitrotoluene as the initial detonator, the fuse passing completely through the cartridge.

^a Berthelot, M., *Sur la force des matières explosives*, t. 2, 1883, p. 183.

^b Lobry de Bruyn, C. A., *Sur l'explosivité de l'azotate d'ammonium*: *Rec. trav. chim. Pays-Bas*, t. 10, 1891, pp. 127-131; Escales, R., *Die Explosivstoffe*, Bd. 4, 1909, p. 40.

^c Lheure, —, *Note sur l'amélioration de la sécurité dans les mines grisouteuses par emploi d'un nouveau dispositif d'amorçage des explosifs*: *Ann. des mines*, sér. 10, t. 12, 1907, p. 169; Escales, R., *Die Explosivstoffe*, Bd. 4, 1909, p. 130.

The temperature of explosion, as calculated from the above reaction, is only $1,121^{\circ}\text{C}.$ * much lower than the calculated temperatures resulting from the usual types of permissible coal-mining explosives, which generally vary between $1,500^{\circ}$ and $2,000^{\circ}\text{C}.$ Its insensitiveness and relatively low explosion pressure, however, prevent pure ammonium nitrate per se from having any practical application as a blasting explosive.

By the admixture of suitable combustible materials, this insensitiveness is overcome and explosives of greater strength are obtained. As has been noted, a large proportion of the explosives which have been placed on the bureau's permissible list are of this type, the list on June 1, 1915, including 61 ammonium-nitrate explosives out of a total of 133 explosives; 14 other ammonium-nitrate explosives formerly on the permissible list have been withdrawn.

The materials used as sensitizers for ammonium nitrate may be (1) explosive or (2) nonexplosive. The first group of sensitizers comprises nitroglycerin, nitrocellulose, nitrosubstitution compounds, or mixtures of two or more of these substances. The second group includes various nonexplosive combustible materials, such as resins, sulphur, carbonized curcuma powder, cereal flour, sugar, hydrocarbon oils or other oils, paraffin, and coal.

HYDRATED EXPLOSIVES.

Under the designation "hydrated explosives" are included those that depend for reduction of their flame temperature largely upon the cooling effect of water in the form of water of crystallization of certain salts included in their composition.

The list of "permissible explosives" included, on June 1, 1915, 6 explosives under this classification and 3 others previously in this class had been withdrawn.

The hydrated salts used in these explosives are Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), or potassium alum [$\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$], containing respectively 51.22 per cent and 45.57 per cent water of crystallization.

Certain explosives included in other classes of "permissible explosives" also contain these hydrated salts, as well as aluminum sulphate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$], with 48.81 per cent of water or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), with 20.92 per cent of water, but not in sufficient quantities to justify their classification as hydrated explosives.

* Hall, Clarence, Snelling, W. O., and Howell, S. P., Investigations of explosives used in coal mines, with a chapter on the natural gas used at Pittsburgh, by G. A. Burrell, and an introduction by C. E. Munroe: Bull. 15, Bureau of Mines, 1912, p. 32. Other calculated values for the temperature of explosion of ammonium nitrate are $1,134^{\circ}\text{C}.$ (Helse) and $1,130^{\circ}\text{C}.$ (French Explosives Commission), given by Escalas, R., *Die Explosivstoffe*, Bd. 4, 1909, p. 47.

The hydrated explosives all contain nitroglycerin as the principal explosive ingredient, and most of them also contain ammonium nitrate and various other components common to explosives of other classes.

ORGANIC NITRATE (OTHER THAN NITROGLYCERIN) EXPLOSIVES.

The "permissible list" on June 1, 1915, included only 3 explosives of this class; 6 others had previously been withdrawn from the list.

This class includes explosives containing nitrostarch* or other organic nitrate as their characteristic ingredient.

Nitrostarch, without the admixture of other ingredients which reduce its brisance and high explosion temperature, and modify other of its properties, is unsuited for use as a coal-mining explosive. The temperature of explosion of nitrostarch containing 12.75 per cent nitrogen is, as calculated by the writer, approximately 2,340° C., which is considerably higher than the explosion temperatures of permissible explosives.^b Furthermore, the products of explosion of nitrostarch include larger amounts of carbon monoxide than are desirable in mining explosives. By suitable additions of oxidizing agents and heat-absorbing materials, it is possible, however, to prepare nitrostarch explosives answering all requirements of permissible explosives.

NITROGLYCERIN EXPLOSIVES.

The classification "nitroglycerin explosives" includes those explosives whose characteristic ingredient is nitroglycerin which are not included in the class of "hydrated explosives."

Of the 133 explosives on the "permissible list," June 1, 1915, 63 were included in this class, and 12 others previously in this class had been withdrawn from the list before that date.

The ingredients used in explosives of this class include practically all those entering into the composition of explosives of the various other classes.

Permissible explosives of the nitroglycerin class may be regarded as modified dynamites, in which any of the general methods mentioned on page 6, or combinations of these methods, may be employed for reducing the amount and temperature of the flame produced by explosion.

* The term "nitrostarch" is used in this bulletin because of its acceptance in general usage. The correct chemical designation is starch nitrate.

^b See Hall, Clarence, Snelling, W. O., and Howell, S. P., Investigations of explosives used in coal mines, with a chapter on the natural gas used at Pittsburgh, by G. A. Burrell, and an introduction by C. E. Munroe: Bull. 15, Bureau of Mines, 1912, p. 28.

PHYSICAL EXAMINATION OF PERMISSIBLE EXPLOSIVES.

Among the requirements which must be met by an explosive in order that it may be classed as a "permissible explosive" are found the following:^a

"An explosive will be considered unsatisfactory if it is not chemically stable, if it shows leakage of nitroglycerin, or if it is in such condition that exudation of nitroglycerin would occur in handling or transportation."

It is therefore important that tests be made on each sample of explosive to determine its stability and liability to exude nitroglycerin. In addition to these tests the determination of gravimetric density is included as part of the physical examination.

DETERMINATION OF GRAVIMETRIC DENSITY.

The determination of gravimetric density or apparent specific gravity of the cartridge of explosive has been already described in a former publication.^b The volume of the entire cartridge is found by determining the amount of uniform sand, of previously determined gravimetric density, displaced by the cartridge. The weight of the cartridge in grams divided by its volume in cubic centimeters gives the apparent specific gravity or gravimetric density of the cartridge.

TESTS FOR LIABILITY OF EXUDATION.

The three general methods for determining the liability of exudation of liquid ingredients from cartridges of an explosive have been described for the ordinary types of dynamites.^c These methods are employed in the same manner for "permissible explosives." The method generally employed in the bureau's laboratory is the centrifugal method, in which 8-gram samples of the explosive, each contained in an ordinary porcelain Gooch crucible without a mat, are centrifuged for 5 minutes at a speed of 600 revolutions per minute, the circle of rotation made by the bottom of the crucibles being 28 centimeters in diameter. Any exuding nitroglycerin is absorbed in a small quantity of cotton placed in an ordinary porcelain crucible suspended beneath the Gooch crucible.

The temperature at which the test is made should be approximately 20° C. Under these conditions a loss of more than 5 per cent of the original weight of the sample is considered by the bureau to indi-

^a Fees for testing explosives, Bureau of Mines, Schedule 1, Sept. 17, 1913, 8 pp.

^b Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite, Bull. 51, Bureau of Mines, 1913, pp. 7-8.

^c Snelling, W. O., and Storm, C. G., Op. cit., pp. 8-10.

cate liability of leakage of nitroglycerin from the cartridges in transportation or storage.

It should be noted, however, that exudation is much less liable to occur in explosives of the "permissible" type than in ordinary grades of dynamite because of the smaller content of nitroglycerin in most explosives of the former class.

TESTS FOR STABILITY.

ABEL TEST.

All samples of explosives submitted to the bureau are tested by the Abel heat test, a full description of which has been published by the bureau.^a Briefly, the test depends upon the time required for the production of a brownish line of discoloration of standard intensity on a strip of potassium iodide-starch paper suspended above the explosive in a glass test tube by the oxides of nitrogen liberated from the explosive when the sample is heated in a water bath at a constant temperature. The test is made in duplicate, on samples weighing 2 grams each, at a temperature of 71° C. $\pm 0.5^\circ$ C. An explosive is considered to be of unsatisfactory stability when the time of the test is less than 10 minutes.

"INTERNATIONAL" 75° TEST.

The "preliminary test" recommended by the international commission which reported to the Eighth International Congress of Applied Chemistry, 1912, on "Methods for Testing the Stability of Explosives,"^b is made use of to supplement the Abel test. This test is made as follows:

METHOD OF MAKING THE TEST.

Two samples of explosive of 10 grams each, without previous drying, are placed in glass tubes 35 mm. in diameter and 50 mm. in height; the tubes are loosely covered with watch glasses and heated for 48 hours in a constant-temperature oven at 75° C.

At the end of this period of heating the samples are examined for signs of decomposition, as indicated by change of appearance or by odor or the presence of nitrous fumes in the tube. The explosive is considered to be of unsatisfactory stability if positive indication of decomposition is noted.

In order to gain additional information as to the behavior of explosives under the conditions of this test, in tests by the bureau the

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite, Bull. 51, Bureau of Mines, 1913, pp. 10-12.

^b Commission Internationale pour L'Etude de L'Unification des Methodes D'Epreuves sur la Stabilité des Explosifs; Rapport, final approuvé le 25 juillet 1912, pour être présenté au VIII^{me} Congrès International: Original Communications, Eighth Int. Cong. App. Chem., vol. 25, September, 1912, p. 261.

tubes containing the samples have been accurately weighed before and after heating at 75° C. and the loss of weight noted in terms of percentage of the weight of original sample. Any marked decomposition of the explosive or of any of its components would be indicated by a considerable loss of weight in excess of the moisture content of the explosive, due consideration being made for the fact that some loss from volatilization of nitroglycerin, or possibly of other constituents, will result during such heating.

COMPARISON OF RESULTS OF "ABEL" AND "INTERNATIONAL" TESTS.

As a general rule, the loss of weight noted in testing stable explosives by this method is but a small amount in excess of the moisture content, the difference being usually less than 0.5 per cent and rarely exceeding 1 per cent. One explosive of doubtful stability, which contained among other ingredients nitroglycerin, potassium chlorate, and ammonium nitrate (a very unusual and dangerous mixture), gave an Abel test of only 7 to 9 minutes, and on being subjected to the "international" 75° test it evolved odors of chlorine and oxides of nitrogen and lost nearly 5 per cent in weight in excess of the moisture content.

A large number of tests made by the "international" method in the bureau's laboratory have substantiated the results of the Abel test.

SAMPLING AND PREPARATION FOR ANALYSIS.

The test requirements provide that samples of 100 pounds of each explosive to be tested for permissibility must be submitted to the bureau by the manufacturer. From this large sample, 4 to 6 cartridges are selected at random for chemical examination. A sample for analysis is prepared by removing the paper wrapper, care being taken that particles of paraffin from the outside of the wrapper do not become mixed with the explosive, cutting off with a horn spatula 3 to 5 cm. of each end of the cartridge and mixing thoroughly the central parts of each cartridge in a porcelain dish with a large horn spoon. The explosive is reduced to a mass of such uniformity as the fineness of the ingredients will permit, all hard masses of particles being broken up by means of the spoon. After very thorough mixing of the sample, a wide-mouthed sample bottle of about 250 c. c. capacity is filled by taking portions with the spoon from different parts of the entire mass in the dish. The sample in the bottle should be remixed immediately before analysis in order to compensate for any segregation of liquid ingredients. Experiments have demonstrated that appreciable segregation may occur in even a few days.*

* Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite, Bull. 51, Bureau of Mines, 1913, pp. 14-15.

QUALITATIVE ANALYSIS.

In order to decide upon the method of quantitative analysis to be followed, it is essential that first a complete qualitative analysis of the explosive should be made. After such examination has shown the identity of the components of the explosive mixture, the proper methods for quantitative separation or determination of these components can then be chosen.

The general methods for the qualitative analysis of permissible explosives are the same as those described in Bulletin 51^a for ordinary types of dynamite. It should be noted, however, that many substances are employed as constituents of the low-flame explosives which are not found in ordinary blasting explosives.

COMPONENTS OF LOW-FLAME EXPLOSIVES.

Below is given a list of some of the substances which have been found in low-flame explosives. Most of them have been identified as constituents of explosives manufactured in this country; a few are ingredients of foreign explosives.

These substances are classified according to their solubility in the general scheme usually followed in analysis.

Some components of low-flame explosives.

Soluble in ether.	Soluble in water.	Sodium sulphate. Sugar.
Asphaltum.	Alum (crystals).	Zinc oxide. ^b
Nitrobenzenes.	Aluminum sulphate (crystals).	Insoluble.
Nitroglycerin.	Ammonium chloride.	Charcoal.
Nitronaphthalenes.	Ammonium nitrate.	Clay.
Nitropolyglycerin.	Ammonium oxalate.	Coal.
Nitrotoluenes.	Ammonium perchlorate.	Corn meal.
Oils (mineral or vegetable).	Ammonium sulphate.	Corncob meal.
Paraffin.	Barium nitrate.	Graphite.
Resins.	Calcium sulphate (crystals).	Kieselguhr.
Sulphur.	Gums.	Nitrated wood.
Vaseline.	Magnesium sulphate (crystals).	Nitrocellulose.
	Potassium bichromate.	Nitrostarch.
	Potassium chlorate.	Peanut-shell meal.
	Potassium nitrate.	Powdered slate.
	Potassium perchlorate.	Rice hulls.
	Potassium sulphate.	Sand.
	Sodium bicarbonate.	Sawdust.
	Sodium carbonate.	Turmeric.
	Sodium chloride.	Vegetable ivory meal.
	Sodium nitrate.	Wheat flour.
		Wood pulp.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite, Bull. 51, Bureau of Mines, 1913, pp. 16-19.

^b Generally found partly or wholly in the water extract owing to its solubility in ammonium-nitrate solutions.

^c Partly soluble in the dilute acid used.

METHOD OF CONDUCTING QUALITATIVE ANALYSIS.

In conducting the qualitative examination of a permissible explosive it is usually advisable to separate its components into groups, as indicated above, by successive extractions with ether, water, and dilute hydrochloric acid (1:10), so that the identification of the various ingredients present is much simplified.

These extractions are conveniently made by shaking a rather large sample (about 25 grams) of the explosive with ether in a large stoppered test tube, filtering the solution through a paper filter and treating the residue once or twice again with fresh ether in the same manner. The ether solution is evaporated, and the insoluble residue, after drying to remove adhering ether, is treated in a similar manner with water, and finally with dilute hydrochloric acid.

SPECIAL QUALITATIVE TESTS.

Tests for some of the more unusual substances, not generally found in the ordinary types of blasting explosives, are made as follows:

TEST FOR NITROPOLYGLYCERIN.

In making a test for nitropolyglycerin the ether extract, after evaporation of the ether, is filtered through a paper filter in order to separate any insoluble oily or resinous materials. Some of the clear filtrate is tested for nitrosubstitution compounds by means of the color test described in Bulletin 51.^a In the absence of nitrosubstitution compounds the filtrate is tested for nitropolyglycerin by determining its solubility in a mixture of 60 parts glacial acetic acid and 40 parts water, as described on page 53. This test readily detects nitropolyglycerin in admixture with nitroglycerin.

TEST FOR MONONITRONAPHTHALENE.

Mononitronaphthalene is readily detected in the residue obtained by evaporation of the ether extract by adding a drop of this material to a mixture of about equal parts of strong sulphuric acid and water. Mononitronaphthalene, if present, causes a brilliant red color.

TEST FOR CHLORIDES, CHLORATES, AND PERCHLORATES.

Chlorides, chlorates, and perchlorates in a mixture are identified as follows: Some of the solution in water is acidified with a few drops of nitric acid, an excess of silver nitrate added, the mixture heated to boiling, shaken well to coagulate the precipitate of silver chloride, and filtered. To the clear filtrate a few cubic centimeters of formaldehyde (40 per cent solution) is added and the mixture is then boiled.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite, Bull. 51, Bureau of Mines, 1913, pp. 17-18.

The formaldehyde reduces any chlorate present to chloride, which is precipitated as silver chloride by the excess of silver nitrate present. The reaction is practically complete if the mixture is allowed to stand on the steam bath for about an hour, although a considerably longer time is required for quantitative reduction.

The precipitate is filtered off and the filtrate evaporated to dryness to remove excess of nitric acid, transferred with a small volume of water to a crucible, enough dry sodium carbonate added to fill the crucible, the mixture dried carefully over a burner, and fused. The fused mass is dissolved in dilute nitric acid. If perchlorates are present, the solution will be found to contain a precipitate of silver chloride.

TEST FOR SUGAR.

The presence of any appreciable quantity of organic substances in the solution in water is indicated by a more than slight charring of the residue, obtained by evaporating the solution, when it is heated over a burner. Sugar is tested for by acidifying some of the water solution with a little dilute hydrochloric acid, heating to boiling in order that any cane sugar present may be inverted, neutralizing with potassium hydroxide, and boiling with Fehling's solution. A precipitation of reduced cuprous oxide indicates the presence of sugar.

TEST FOR GUM ARABIC.

Gum arabic is precipitated by the addition of a solution of basic lead acetate to the water extract. (See quantitative determination of gum arabic, p. 67.)

TEST FOR NITROSTARCH.

Nitrostarch in the residue left after extracting the water-soluble ingredients is detected by examining a small portion of the residue under the microscope. (See p. 74.) Nitrostarch is readily distinguished from unnitrated starch by moistening the residue under the microscope with a drop of solution of iodine in potassium iodide; the unnitrated starch granules are colored dark blue by the iodine solution, whereas nitrostarch granules are not affected.

TEST FOR NITROCELLULOSE.

Nitrocellulose is readily distinguished from nitrostarch by means of the microscope, but when present in small amounts may be overlooked. The dried residue insoluble in water should be treated with acetone and the acetone extract poured into hot water in order to volatilize the acetone and precipitate any dissolved nitrocellulose. The white precipitate may be dried and identified as nitrocellulose or nitrostarch by its rapid burning on being ignited with a flame. Of

course, this last test will not distinguish between nitrocellulose and nitrostarch.

IDENTIFICATION OF WOOD PULP MIXED WITH CEREAL PRODUCTS.

The following test devised by Le Roy^a has been found valuable for the identification of small amounts of wood pulp mixed with various cereal products.

One gram of phloroglucinol is dissolved in 15 c. c. of ethyl alcohol (90 to 95 per cent) and 10 c. c. of sirupy phosphoric acid is added. Then 0.5 c. c. of this reagent is rubbed with a little of the sample in a porcelain dish. The wood fibers quickly become colored a rose tint, gradually turning to carmine.

This test was tried by the author on coarse and fine wheat flour and on corn meal with negative results. A very small proportion of wood pulp mixed with these cereals was indicated by red spots throughout the mixture. Examination under the microscope showed that each fiber of the wood pulp was colored a bright carmine, whereas the starch granules and cereal fibers were unchanged in color.

Less than 0.5 per cent of wood pulp in an explosive containing 36 per cent of corn meal was readily detected. Such amounts of wood pulp may enter into the composition of an explosive from imperfect cleaning of the mixing bowl after a previous mixing.

IDENTIFICATION OF WHEAT FLOUR AND CORN MEAL.

The following tests^b have been found of assistance in distinguishing between finely ground white corn meal and coarse wheat flour:

GLYCERIN TEST.

About 1 gram of the material is treated with 15 c. c. of glycerin and boiled for a few minutes. Corn is indicated by the well-known pop-corn odor.

This test was tried separately on both corn meal and wheat middlings. At first the difference in odor was hardly appreciable, but after a few minutes of boiling the wheat darkened to a brown color and gave an unpleasant "burnt" odor, whereas the corn meal continued to evolve the pleasant odor of pop corn.

ALKALI TEST.

A small quantity of the material is treated with 10 c. c. of a 1.8 per cent solution of potassium hydroxide and allowed to stand for about two minutes in a test tube; it is then made nearly neutral with

^a Le Roy, G. A., Recherche de la sciure (fleurage) de bois dans les farines: Ann. chim. anal., t. 4, 1899, p. 221; Allen, A. H., Commercial organic analysis, vol. 1, 1905, p. 462.

^b Allen, A. H., Loc. cit.

dilute hydrochloric acid. The formation of a stiff, gelatinous mass indicates wheat starch, whereas cornstarch is not altered.

This test and the glycerin test are of use mainly when the residue left after extraction with water contains no ingredients other than wheat flour or corn meal.

MECHANICAL SEPARATION OF SOLID INGREDIENTS.

It is frequently difficult, in analyzing a permissible explosive that contains a number of water-soluble ingredients, to ascertain definitely the manner in which the various acid and basic ions, found in the water extract by qualitative tests and quantitatively determined by gravimetric or volumetric methods, were combined in the original explosive. The difficulties are similar to those encountered in reporting the results of water analyses. The water analyst usually solves the difficulty by reporting the positive and negative ions separately without attempting to determine their actual combinations. It is necessary, however, that the report of the analysis of a permissible explosive should give definite information as to the various salts present.

As an instance of such mixtures, a solution giving tests for Na, NH_4 , Cl, and NO_3 , may be examined quantitatively and the amount of each of these ions present accurately determined, without definite knowledge being obtained as to whether the salts contained in the water solution were (a) NaNO_3 , NH_4NO_3 , NaCl and NH_4Cl , or (b) NaNO_3 and NH_4Cl , or (c) NH_4NO_3 and NaCl .

Although chemical analysis of such a water extract offers no means of determining its true composition, the writer has found that it is often possible to gain considerable information by a mechanical separation of the original solid ingredients before dissolving in water. Such mechanical separation is facilitated by the fact that the ingredients of explosives are frequently not finely pulverized in the course of manufacture.

SEPARATION OF INGREDIENTS BY SCREENING.

The separation is carried out as follows:

A sample of 25 to 50 grams of the original explosive is washed several times with ether in order to remove the nitroglycerin, oily materials, or other ether-soluble substances; the residue is dried a short time until the adhering ether has evaporated, and then sifted through a set of sieves. The coarser sieves (10 and 20 mesh) will usually be found to retain more or less material consisting of coarse fragments of wood pulp or other carbonaceous absorbent, together with coarse crystals of the water-soluble ingredients that have escaped pulverization or have purposely been incorporated in a coarse

condition. This coarse material is spread out on a piece of glazed paper and crystals of similar appearance sorted out by the aid of a pair of forceps. A few fragments or crystals of each kind may be separately tested qualitatively and readily identified. Much information can often be gained by dissolving a single crystal in a drop of water on a microscope slide, allowing the water to evaporate, and examining the resulting crystals under the microscope, with or without the polarizing attachment. Many substances are easily identified in this manner. A single crystal may be dissolved in 1 or 2 c. c. of water, the solution divided into several small parts, and separate tests made on each part, a process which may serve absolutely to identify the crystal.

Among many instances in which mechanical separation has been useful are the following:

1. An explosive contained, among other ingredients, ammonium nitrate, ammonium sulphate, crystallized potassium alum, potassium sulphate, and coal. By sifting and picking over the coarser crystals, coal, alum, ammonium nitrate, and ammonium sulphate were separated and positively identified.

2. From another explosive, sodium nitrate, ammonium nitrate, crystallized magnesium sulphate, and corn meal were separated and identified.

3. From a third explosive, crystalline trinitrotoluene, alum, and ammonium nitrate were isolated.

In each of these instances the identification of these constituents enabled the actual composition of the mixtures to be calculated from the results of the quantitative analysis without "guesswork" as to the manner in which the various bases and radicles were combined.

SPECIFIC-GRAVITY SEPARATION OF INGREDIENTS.

Another method, which is much used in the bureau's laboratory, for the identification of the various components of such mixtures as those mentioned depends on the fact that the different components differ in specific gravity. This method, which has been described in Technical Paper 78^a of the bureau, is briefly summarized here. The separation is effected in a mixture of bromoform (specific gravity 2.83) and chloroform (specific gravity 1.49). These liquids are miscible in all proportions, and yield liquid mixtures of any desired density between the limits of their respective specific gravities. The various salts used in blasting explosives are insoluble in such mixtures, and the specific gravities of these salts lie mostly between 1.50 and 2.50, a range which is entirely covered by the possible bromoform-chloroform mixtures.

^a Storm, C. G., and Hyde, A. L., Specific-gravity separation applied to the analysis of mining explosives: Tech. Paper 78, Bureau of Mines, 1914, 14 pp.

A series of these liquid mixtures is prepared, with specific gravities of 1.60, 1.77, 1.89, 1.98, 2.16, etc., respectively. The specific gravities mentioned have been found especially useful, but obviously any desired mixture within the limits mentioned may be prepared. These mixtures can be used repeatedly, being filtered back into the original bottles after use. Their specific gravities should be checked from time to time.

A sample of the original explosive to be tested is extracted several times with ether to remove all liquid ingredients, dried thoroughly in an oven, and then some of the dry material is shaken with a quantity of one of the bromoform-chloroform mixtures in a small separatory funnel provided with a wide-bore stopcock. On standing a short time, the mixture being carefully stirred meanwhile with a thin glass rod so as to liberate any entangled air bubbles, the solid substances separate into two layers, the heavier crystals settling to the bottom and the lighter crystals and carbonaceous material collecting as a layer in the upper part of the liquid.

The heavier salt may be drawn off into a dish or beaker by quickly opening the cock and again closing it before the lighter solids begin to come through. The greater part of the liquid drawn off is decanted back into the funnel, and the heavy crystals dried and examined by means of qualitative tests.

It may also be found possible to separate a part of the lighter salt from the carbonaceous material by further treatment in a similar manner with a liquid of less density than the one first used.

The specific gravities of some of the more common salts that may be present are as follows:^a

Specific gravities of salts occurring in explosives.

Salt.	Specific gravity.	Temperature.	Authority.
		°C.	
Ammonium alum (crystals).....	1.62		Clarke, F. W.
Ammonium chloride.....	1.62		Schröder.
Ammonium nitrate.....	1.74		Do.
Ammonium perchlorate.....	1.87		Woulf.
Ammonium sulphate.....	1.77	20	Retgers.
Barium nitrate.....	3.23		Clarke, F. W.
Calcium carbonate (precipitated).....	2.73		Rose, G.
Calcium sulphate (anhydrous).....	2.97		Schröder.
Calcium sulphate+2H ₂ O.....	2.32		Clarke, F. W.
Magnesium carbonate.....	3.04		Schröder.
Magnesium sulphate+7H ₂ O.....	1.68		Clarke, F. W.
Magnesium sulphate (anhydrous).....	2.65		Do.
Manganese dioxide.....	5.03		Retgers.
Potassium alum (crystals).....	1.75	17	Do.
Potassium chlorate.....	2.33		Clarke, F. W.
Potassium chloride.....	1.99	16	Retgers.
Potassium nitrate.....	2.09		Clarke, F. W.
Potassium perchlorate.....	2.52		Schröder.
Potassium sulphate.....	2.66	20	Tutton.
Sodium chloride.....	2.17	17	Retgers.
Sodium nitrate.....	2.26		Clarke, F. W.
Sodium sulphate (anhydrous).....	2.66		Do.
Sodium sulphate+10H ₂ O.....	1.46		Do.

^a Landolt and Börnstein, *Physikalisch-chemische Tabellen*, pp. 230-251.

It is necessary that the specific gravity of the liquid mixture used should be at least about 0.1 less than that of the salt which it is desired to separate from lighter ingredients. The separation is never complete because of the buoyant effect of air bubbles and of particles of wood pulp or other carbonaceous materials, which adhere to the heavier crystals.

EXAMPLE OF USEFULNESS OF METHOD.

The following is an example of the usefulness of the method of specific-gravity separation as applied to an ordinary type of permissible explosive: The solution from treatment of the explosive with water was found by the usual qualitative tests to contain NH_4 , Na, NO_3 , and Cl. Qualitative and quantitative determinations failed to show the manner in which the acid and basic radicles were combined, that is, whether the salts present were NaNO_3 and NH_4Cl , NaCl , and NH_4NO_3 , or a mixture of all four of these substances. On applying the specific-gravity method, using a liquid mixture of 1.8 specific gravity, crystals of NaNO_3 sank to the bottom, were drawn off, and identified. NaCl , if present, would have been found with the NaNO_3 , but no test for Cl was obtained. The lighter portion of the salts gave strong qualitative tests for NH_4 , Cl, and NO_3 . It was therefore established that the explosive contained a mixture of NaNO_3 , NH_4NO_3 , and NH_4Cl .

MICROSCOPIC EXAMINATION.

The use of the microscope in identifying constituents of the insoluble residue is discussed on page 74.

Much information is frequently obtained as to the identity of the constituents of an explosive by examining a sample of the original explosive under relatively low magnification by the aid of the binocular microscope. In some explosives it is possible to identify as many as four or five constituents by a rapid examination under the microscope. Familiarity with the form and appearance of the various crystalline and noncrystalline substances used in explosives is, of course, essential, and such familiarity can best be obtained by a study, under the microscope, of samples of these different substances.

Single fragments of crystals may be dissolved in a drop of water and the solution allowed to evaporate slowly on a microscope slide, in order to obtain perfectly formed crystals of the substance to be identified.

QUANTITATIVE ANALYSIS.

It has been shown in the discussion of the general characteristics of permissible explosives of the different classes (pp. 7 to 10) that most of the ingredients used in the explosives of any class may be found in the explosives of any other class. A separate discussion of the methods of analysis used for explosives of each class would therefore involve much useless repetition. In general, the analysis of any permissible explosive is carried out by successive extractions of a suitable sample of the explosive with different solvents, usually ether, water, dilute hydrochloric acid, or other liquids which act as solvents only, each of the solutions obtained being designed to contain one or more unchanged components of the explosive. The components thus separated from the mixture are then analyzed to determine the proportion of each in the explosive.

The general method of procedure is therefore quite similar to that employed in the analysis of the ordinary types of dynamite, described in Bulletin 51,^a although the introduction of components not found in ordinary dynamites increases the difficulties of analyzing explosives of the permissible type.

DETERMINATION OF MOISTURE.

The amount of moisture in ammonium-nitrate explosives is usually small. Obviously, water is never intentionally added to explosives of this type for the purpose of reducing the temperature of explosion. Because of the hygroscopic nature of ammonium nitrate, and the fact that its insensitiveness is increased by the absorption of moisture, all ingredients of explosives containing ammonium nitrate are generally well dried. About 75 per cent of the explosives of this type tested by the bureau have contained less than 1 per cent of moisture.

The moisture content of the nitroglycerin explosives may be rather high, as the addition of water is one of the means frequently employed for reducing the flame temperature of such explosives. The moisture content of some of the permissible explosives of this type is as high as 10 per cent.

The determination of moisture in permissible explosives of all classes is made by the method described in Bulletin 51.^b A sample weighing approximately 2 grams is spread evenly over the surface of a 2-inch watch glass and desiccated over sulphuric acid for three days at a room temperature as near 20° C. as possible. The loss of weight is considered as moisture.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 16-50.

^b Snelling, W. O., and Storm, C. G., op. cit., p. 29.

FACTORS AFFECTING RESULTS OF MOISTURE DETERMINATION.

The extent to which these results are affected by variations in temperature, weight of sample, exposed surface of sample, quantity and strength of acid, type of desiccator, and other conditions have been considered in Bulletin 51.^a

The accuracy of the results obtained in determining moisture by desiccation also depends on the absence of any other ingredients from the explosive that could be lost during desiccation.

The principal ingredients whose volatility may influence the results are nitroglycerin, some of the nitrosubstitution compounds, and combined water in substances containing water of crystallization.

EFFECT OF VOLATILITY OF NITROGLYCERIN.

It has been demonstrated by experiments described in Bulletin 51^b that there is a continual loss of nitroglycerin from explosives containing this ingredient, during the determination of moisture by desiccation; that this loss varies with the temperature; and that it is impossible to bring such a sample to constant weight under ordinary conditions of determination.

It is believed, however, that in desiccation for three days under the conditions above described the amount of nitroglycerin volatilized is inappreciable.

ILLUSTRATIVE EXPERIMENT.

To illustrate the fact that nitroglycerin is appreciably volatile at ordinary temperatures and that its volatility increases with the temperature, an experiment was described in Bulletin 51^c in which 2 grams of a "60 per cent" dynamite was spread on a 3-inch watch glass, dried over sulphuric acid for three days to remove moisture, and then placed in an empty desiccator containing no drying agent, the desiccator being placed in an incubator oven at a constant temperature of 33° to 35° C. The sample was weighed at intervals and the loss of weight noted. The results are shown by the curve in figure 1.

Since the publication of the bulletin mentioned additional weighings of the sample have been made, covering a total period of 459 days. After the last weight was taken the sample on the watch glass was analyzed in order to determine whether the total loss of weight could be accounted for by the actual loss of nitroglycerin as determined by analysis.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 19-27.

^b Snelling, W. O., and Storm, C. G., op. cit., pp. 24-26.

^c Snelling, W. O., and Storm, C. G., op. cit., pp. 26, 27.

The entire data of the experiment are shown in the following table:

Effect of heating "60 per cent" dynamite in an empty desiccator at 33° to 35° C. for 459 days.

Time in desiccator.	Loss of weight.	Time in desiccator.	Loss of weight.
<i>Days.</i>	<i>Per cent.</i>	<i>Days.</i>	<i>Per cent.</i>
4	0.13	77	5.35
7	.46	202	9.33
10	.80	243	11.13
13	1.10	331	13.32
16	1.40	418	16.75
20	1.75	459	17.52
41	3.40		

The weight of the dried sample at the time of beginning the heating in the empty desiccator was 1.9720 grams; its final weight after

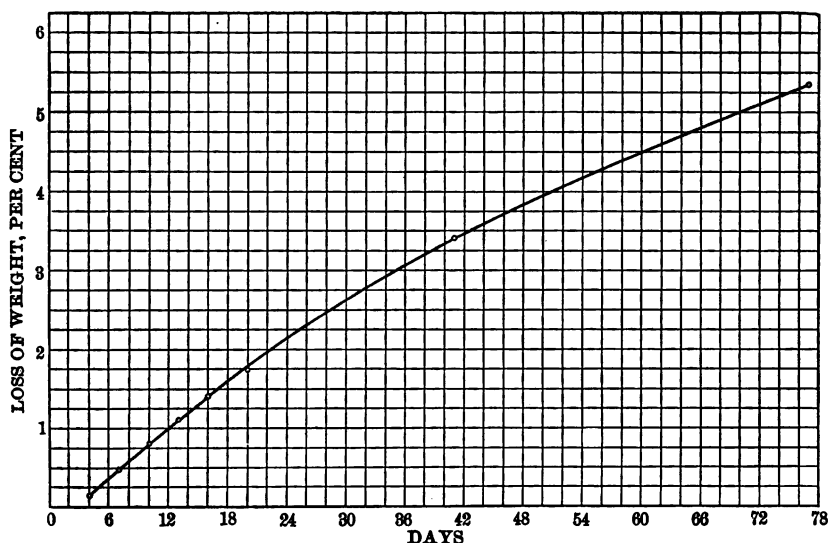


FIGURE 1.—Result of exposing dry "60 per cent" dynamite for 77 days in desiccator at 33° to 35° C. without desiccating agent.

459 days' heating was 1.6265 grams, a total loss of 0.3455 gram. The original dry sample contained 60.26 per cent, or 1.1883 grams, of nitroglycerin, whereas after heating for 459 days, only 0.8355 gram of nitroglycerin was found by analysis, showing a loss of 0.3528 gram of nitroglycerin. This figure agrees fairly well with the actual loss of weight, 0.3455 gram.

To summarize the results of this experiment, about one-third of the total quantity of nitroglycerin originally present was lost by exposure to a temperature of 33° to 35° C. for 459 days. The uni-

formity of the rate of loss is indicated by the curve in figure 2. Complete analysis of the sample showed that no change other than loss of nitroglycerin had occurred.

There is no doubt that the loss of nitroglycerin was due to volatilization and not to decomposition. On several occasions when the desiccator was opened to weigh the sample, a piece of potassium iodide-starch paper was at once exposed to the atmosphere within the desiccator, but in no case was any reaction for oxides of nitrogen obtained, nor could any odor of decomposition products be detected.

After the completion of the experiment the interior walls of the empty desiccator were washed with sulphuric acid and this acid transferred to the nitrometer in order to test it for the presence of nitroglycerin. A small amount of NO generated (insufficient for a reading) indicated the presence of nitroglycerin on the walls of the

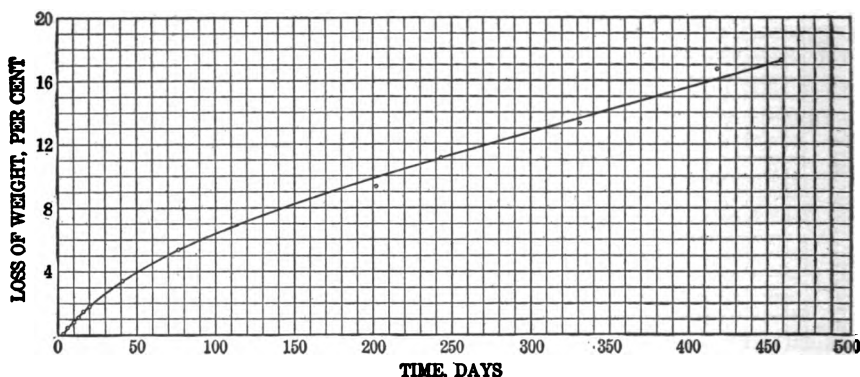


FIGURE 2.—Results of exposing "60 per cent" dynamite for 459 days in desiccator at 33° to 35° C. without desiccating agent.

desiccator, but most of the nitroglycerin volatilized from the dynamite sample had apparently escaped from the desiccator.

EFFECT OF VOLATILITY OF NITROTOLUENES.

The volatility of certain of the nitrosubstitution compounds may also have some effect on the results of the determination of moisture by desiccation. In order to investigate this point experiments were made on the more commonly used nitrotoluenes. The samples were desiccated over sulphuric acid for a number of days and the loss of weight noted at intervals.

The nitrotoluenes used for the tests were of the grade generally used in blasting explosives in this country. The "liquid" dinitrotoluenes and trinitrotoluenes are mixtures containing chiefly dinitrotoluenes and trinitrotoluenes, with more or less mononitrotoluene. Sample A, "liquid trinitrotoluene," contained only a trace of mono

compound, sample C, "liquid dinitrotoluene," contained 11.36 per cent of mono compound.

VOLATILITY OVER SULPHURIC ACID IN ORDINARY DESICCATORS.

The results of these experiments are given in the following tables. Similar samples are uniformly designated by letter, as A, B, C, throughout the tables and descriptions of tests:

Volatility of nitrotoluenes in desiccators in presence of sulphuric acid.

(Samples spread on watch glasses).

Sample.	Designation of sample. ^a	Test No.	Original weight of sample.	Loss in weight after desiccation for—				
				1 day.	3 days.	4 days.	7 days.	11 days.
Mononitrotoluene (ortho).	G	1	<i>Grams.</i> 3.72	<i>Gram.</i> 0.0405	<i>Gram.</i> 0.0766	<i>Gram.</i> 0.1521	<i>Gram.</i> 0.2225	<i>Gram.</i> 0.2834
Do.	G	2	8.31	.0341	.0656	.1197	.3091	.5426
Dinitrotoluene (crystals), melting point 66° to 68°	F	3	1.00	.0014	.00150030	.0004
C.								
Trinitrotoluene (crystals), melting point 81° to 82°	E	4	1.00	.0010	.0010
C.								
"Liquid dinitrotoluene" ^b	C	5	5.73	.0082	.0203	.0279	.0548	.0864
Do.	C	6	6.56	.0085	.0212	.0268	.0512	.0818
"Liquid trinitrotoluene" ^c	A	7	1.8539	.0033	.00370050	.0060

^a Uniform throughout this and other tables.

^b Commercial designation. Substance contains a trace of mononitrotoluene.

^c Contains 11.36 per cent mononitrotoluene.

The results show that crystalline trinitrotoluene does not volatilize appreciably on desiccating; that crystalline dinitrotoluene is very slightly volatile, but the loss in three days is negligible; and that mononitrotoluene (ortho), on the other hand, is appreciably volatile, so that its presence in an explosive would introduce an error in the determination of moisture. The slight volatility of the liquid trinitrotoluene, and the considerably greater volatility of the liquid dinitrotoluene, are probably largely due to the content of mononitrotoluene in each.

EFFECT OF SURFACE AREA OF SAMPLE ON VOLATILITY OF NITROTOLUENES.

The effect of the surface area of the sample exposed in the desiccator was shown in the case of the liquid nitrotoluenes by distributing each sample over a layer of sand spread uniformly on a watch glass.

In the following determinations approximately 10 grams of dry (60-mesh) sand was spread on each watch glass and approximately 3 grams of the liquid sample allowed to drop onto the sand so that it was entirely moistened, but no accumulations of liquid were visible. The watch glasses were then placed in separate desiccators over sulphuric acid and weighed at intervals of two days.

Results of desiccation of liquid nitrotoluenes.

[Samples distributed over sand and placed in desiccators over sulphuric acid.]

Sample.	Sample No. ^a	Test No.	Original weight of sample.	Loss in weight after desiccation for—			
				2 days.	4 days.	6 days.	8 days.
Mononitrotoluene (ortho).....	G	1	<i>Grams.</i> 3.3767	<i>Gram.</i> 0.1793	<i>Gram.</i> 0.3138	<i>Gram.</i> 0.4303	<i>Gram.</i> 0.5421
Do.....	G	2	2.9936	.1745	.3725	.4849	.5840
Dinitrotoluene ("liquid").....	C	3	3.6967	.0276	.0530	.0830	.1096
Do.....	C	4	3.0982	.0281	.0531	.0754	.0984
Trinitrotoluene ("liquid").....	A	5	3.2256	.0071	.0143	.0161	.0225
Do.....	A	7	3.3519	.0064	.0137	.0159	.0214

* Uniform throughout this and other tables.

These results show that with an increase in the surface of the liquid exposed in the desiccator the rate of loss increases.

VOLATILITY OVER SULPHURIC ACID IN VACUUM DESICCATORS.

The volatility of nitrotoluenes when exposed in vacuum desiccators containing sulphuric acid was also investigated. Experiments were made on both crystalline and liquid dinitrotoluenes and trinitrotoluenes, but not on mononitrotoluene, there being no doubt in regard to the ready volatility of mononitrotoluene in a vacuum.

Samples of 1 gram each were weighed in small low-form beakers, and each beaker was placed in a separate Hempel vacuum desiccator containing fresh sulphuric acid. The sample of "liquid dinitrotoluene" (C) contained 11.36 per cent mononitrotoluene, the sample of "liquid trinitrotoluene" (B) contained 2.33 per cent mononitrotoluene, whereas the "liquid trinitrotoluene" (A) contained only a trace of mono compound. At intervals, as indicated in the table, the vacuum was relieved and the samples weighed.

The results were as follows:

Loss of weight of nitrotoluenes in vacuum desiccators.

[Quantity of sample taken for analysis, 1 gram.]

Time sample was exposed.	Loss in weight.				
	Trinitrotoluene ^a (crystals) (E).	Trinitrotoluene ("liquid") (A).	Trinitrotoluene ("liquid") (B).	Dinitrotoluene ("liquid") (C).	Dinitrotoluene ^b (crystals) (F).
<i>Days.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
1.....	0.0007	0.0020	0.0050	0.0199	0.0028
2.....	.0007	.0050	.0104	.0471	.0064
4.....	.0007	.0076	.0174	.0631	.0074
5.....		.0082	.0198	.0939	.0095
6.....		.0093	.0225	.1023	.0112
7.....		.0105	.0253	.1076	.0126
9.....		.0125	.0289	.1161	.0152
10.....		.0135	.0300	.1182	.0188
11.....		.0140	.0318	.1216	.0205
12.....		.0145	.0330	.1240	.0225
13.....		.0150	.0339	.1260	.0241
14.....		.0155	.0363	.1290	.0256

^a Melting point, 81° to 82° C.^b Melting point, 66° to 68° C.

The fact that the loss from pure crystalline trinitrotoluene is no greater than its probable moisture content, and that pure dinitrotoluene undergoes only a slight volatilization, whereas the loss in the case of the liquid materials is greater as the known content of mononitrotoluene is greater, indicates that the volatility of the "liquid nitrotoluenes" is due partly to loss of mononitrotoluene and partly to loss of dinitrotoluene. These results confirm the results of desiccation in ordinary desiccators.

After the 14 days' desiccation the samples of liquids were again examined for mononitrotoluene with the following results: "Liquid trinitrotoluene" (A), none; "liquid trinitrotoluene" (B), 0.83 per cent; "liquid dinitrotoluene" (C), 1.39 per cent.

As a further point of interest the above vacuum-desiccation experiments were repeated on the "liquid trinitrotoluene" (B) and on the "liquid dinitrotoluene" (C), in order to determine whether the mononitrotoluene could be entirely removed from them by continued treatment.

The results of these tests are shown in the table following.

Loss of weight of "liquid nitrotoluenes" in vacuum desiccators.

[Quantity taken for analysis, 1 gram.]

Period of exposure.	Loss in weight.				Period of exposure.	Loss in weight.			
	Trinitrotoluene (liquid). (B).		Dinitrotoluene (liquid). (C).			Trinitrotoluene (liquid). (B).		Dinitrotoluene (liquid). (C).	
Days.	Gram.	Per cent.	Gram.	Per cent.	Days.	Gram.	Per cent.	Gram.	Per cent.
1.....	0.0022	0.22	0.0159	1.59	17.....	0.0297	2.97	0.1251	12.51
3.....	.0044	.44	.0382	3.82	19.....	.0317	3.17	.1298	12.98
5.....	.0065	.95	.0623	6.23	21.....	.0360	3.60	.1348	13.44
7.....	.0132	1.32	.0829	8.29	25.....	.0432	4.32	.1414	14.18
10.....	.0187	1.87	.1036	10.36	27.....	.0448	4.48	.1434	14.34
11.....	.0208	2.08	.1080	10.80	29.....	.0474	4.74	.1461	14.61
13.....	.0238	2.38	.1156	11.56	31.....	.0504	5.04	.1502	15.02
15.....	.0272	2.72	.1209	12.09					

After 31 days of vacuum desiccation these samples were found to contain no mononitrotoluene. The total loss from each sample was, however, considerably greater than the amount of mononitrotoluene originally present, and, furthermore, the fact that constant weight was not obtained even after all of the mono compound had volatilized indicated a slight volatility of other ingredients of these liquid mixtures.

The curves in figure 3 indicate graphically the rate of loss of each of the two samples tested.

DETERMINATION OF MOISTURE IN EXPLOSIVES CONTAINING "LIQUID NITROTOLUENES."

A series of experiments was made to determine the extent to which the results of the usual methods for determining moisture in explosives are affected by the presence of the more or less volatile "liquid

nitrotoluenes." For this investigation a large sample (about 250 grams) of ordinary 45 per cent nitroglycerin dynamite was thoroughly mixed in a large porcelain dish and divided into five 50-gram parts, each of which was placed in a smaller porcelain dish. These five samples were then treated as follows:

1. Five grams of mononitrotoluene (ortho) was added, drop by drop, to sample 1 in such a manner as to distribute it through the sample as thoroughly as possible. The sample was then well mixed with a porcelain spoon and placed in a bottle.

2. Five grams of "liquid dinitrotoluene" (C), with a mononitrotoluene content of about 11 per cent, was added to sample 2 in the manner described for sample 1.

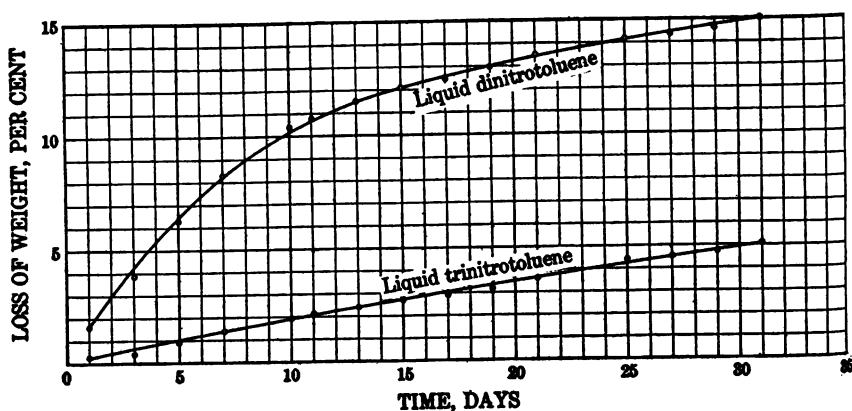


FIGURE 3.—Result of exposure of "liquid nitrotoluenes" in vacuum desiccators.

3. Five grams of "liquid dinitrotoluene" (D), with a mononitrotoluene content of about 4 per cent, was added as described above.

4. Five grams of "liquid trinitrotoluene" (A), practically free from mononitrotoluene, was added as described above.

5. No addition was made to sample 5, but it was mixed in the same manner as the other samples, so that the exposure to the atmosphere would be the same in each test. This sample was used for comparison with samples 1 to 4.

Moisture determinations were then made on each of these five samples (1) by desiccating over sulphuric acid in ordinary desiccators and (2) by desiccating over sulphuric acid in Hempel vacuum desiccators. The weight of the sample used for the determinations was 2.2 grams for samples 1 to 4, inclusive, and 2 grams for sample 5; samples 1 to 4 contained 0.1 gram of nitro compound for each gram of the dynamite. It was therefore assumed that any loss of weight in samples 1 to 4 greater than that of sample 5 was due to volatility of the nitro compounds. Each sample was placed in a separate desiccator.

The results of the determinations were as follows:

Loss in weight of "liquid nitrotoluenes" on desiccation over H_2SO_4 in ordinary desiccators.

Sample No.	Loss in weight after desiccation for—			Sample No.	Loss in weight after desiccation for—		
	3 days.	4 days.	6 days.		3 days.	4 days.	6 days.
1.....	Gram. 0.0795	Gram. 0.0860	Gram. 0.1055	4.....	Gram. 0.0400	Gram. 0.0400	Gram. 0.0405
2.....	.0405	.0430	.0486	5.....	.0380	.0390	.0410
3.....	.0400	.0400	.0410				

Loss in weight of "liquid nitrotoluenes" on desiccation over H_2SO_4 in Hempel vacuum desiccators.

Sample No.	Loss in weight after desiccation for—					Sample No.	Loss in weight after desiccation for—				
	1 day.	2 days.	3 days.	4 days.	6 days.		1 day.	2 days.	3 days.	4 days.	6 days.
1.....	Gram. 0.1185	Gram. 0.1915	Gram. 0.2255	Gram. 0.2410	Gram. 0.2530	4.....	Gram. 0.0392	Gram. 0.0422	Gram. 0.0442	Gram. 0.0457	Gram. 0.0472
2.....	.0450	.0545	.0620	.0685	.0733	5.....	.0380	.0410	.0440	.0475	.0514
3.....	.0480	.0550	.0590	.0620	.0710						

These results show plainly that orthonitrotoluene is readily lost from explosives during the ordinary determination of moisture, causing the results to be abnormally high. In three days' desiccation in an ordinary desiccator, the loss of orthonitrotoluene was about equal to the amount of moisture present in the sample, and in four to six days' desiccation in vacuum, the total loss was equal to the sum of the actual amounts of moisture and orthonitrotoluene present.

The liquid dinitrotoluenes do not appreciably affect the result of the moisture determination in ordinary desiccators. In vacuum desiccators the error is small if the weighing is made at the end of 24 hours, whereas for longer periods of desiccation the loss increases gradually, and is greater as the content of mononitrotoluene in the "liquid dinitrotoluene" is greater.

"Liquid trinitrotoluene" does not affect the results in either ordinary or vacuum desiccators.

These determinations confirm the results obtained by desiccation of the nitrotoluenes alone, but are considered as indicating more exactly the behavior of these ingredients in explosives and their actual influence on the results of the moisture determination.

EFFECT OF VOLATILITY OF MONONITROBENZENE.

Mononitrobenzene is seldom used in blasting explosives because of its high degree of volatility; in fact, it is a constituent of only one of the explosives now on the "permissible" list, and in this

explosive is present in very small quantity. That its presence in an explosive would seriously affect the results of the moisture determination was shown by the following experiments:

Ten grams of mononitrobenzene that was exposed on a 3-inch watch glass in an ordinary sulphuric-acid desiccator lost 0.317 gram in 1 day, 0.702 gram in 3 days, and 2.543 grams in 10 days.

A similar sample that was desiccated over CaCl_2 lost 0.092 gram in 1 day, 0.197 gram in 3 days, and 0.386 gram in 10 days.

A sample distributed over sand on a watch glass and exposed for 10 days over sulphuric acid lost about 40 per cent in weight, and over calcium chloride about 20 per cent.

In a vacuum desiccator with sulphuric acid mononitrobenzene was completely volatilized, 10 grams on a watch glass evaporating completely in 10 days, and 2.5 grams spread over a layer of sand evaporating completely in 3 days.

EFFECT OF MATERIALS CONTAINING WATER OF CRYSTALLIZATION.

Salts containing water of crystallization effectually prevent any reliable determination of moisture by the usual method of desiccation, because all of such salts as are commonly used in explosives lose a portion of their water of crystallization on exposure to a dry atmosphere, and it is impossible to differentiate between the loss due to evaporation of hygroscopic moisture and that due to water of crystallization.

RESULTS OF TESTS WITH MAGNESIUM SULPHATE AND POTASSIUM ALUM.

Tests were made with pure crystallized magnesium sulphate and potassium alum to determine whether any definite proportion of the water of crystallization would be removed by desiccation over either sulphuric acid or calcium chloride.

The percentage loss of weight according to the number of molecules of water lost should be as follows:

Theoretical loss of weight from magnesium sulphate and potassium alum for each molecule of water lost.

Number of molecules of H_2O lost.	Theoretical loss in weight.		Number of molecules of H_2O lost.	Theoretical loss in weight.	
	$\text{KAl} \cdot (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$		$\text{KAl} \cdot (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
	<i>Per cent.</i>	<i>Per cent.</i>		<i>Per cent.</i>	<i>Per cent.</i>
1.....	3.79	7.30	7.....	26.53	51.10
2.....	7.58	14.60	8.....	30.32	
3.....	11.37	21.90	9.....	34.11	
4.....	15.16	29.20	10.....	37.90	
5.....	18.95	36.50	11.....	41.69	
6.....	22.74	43.80	12.....	45.48	

Samples of these salts were ground to pass a 20-mesh sieve, exposed on watch glasses in desiccators, and the loss of weight noted. The results were as follows:

Loss of weight from magnesium sulphate and potassium alum on desiccation over sulphuric acid and calcium chloride.

Time of desiccation.	Loss of weight.			
	$KAl(SO_4)_2 \cdot 12H_2O$.		$MgSO_4 \cdot 7H_2O$.	
	Over H_2SO_4 .	Over $CaCl_2$.	Over H_2SO_4 .	Over $CaCl_2$.
Days.	Per cent.	Per cent.	Per cent.	Per cent.
3.....	8.68 to 9.86	3.42 to 3.94	14.15 to 14.51	9.32 to 9.87
8.....		13.41 to 14.96	25.72 to 29.11	14.71 to 18.35
9.....	28.08 to 30.84			
12.....		17.90 to 20.05		19.77 to 20.55

DISCUSSION OF RESULTS OF EXPERIMENTS.

The above results indicate the impossibility of correcting the total loss of weight found by desiccating an explosive containing salts carrying water of crystallization for the amount of such water of crystallization lost by a given treatment.

Furthermore, it is apparent that it is impossible to determine the total hygroscopic moisture plus water of crystallization by drying in an oven at temperatures higher than atmospheric, because under such conditions other ingredients, such as nitroglycerin and ammonium nitrate, would be more or less volatilized.

It is therefore necessary to determine all constituents other than moisture by direct methods and estimate the content of water by difference. In other words the remainder obtained by deducting the sum of all constituents other than water from 100 per cent is assumed to be the total water content of the explosive. For this purpose the constituent to which the water of crystallization belongs may be calculated as containing its full quota of water of crystallization (for example, magnesium sulphate as $MgSO_4 \cdot 7H_2O$), and the difference from 100 per cent reported as moisture, or the crystallized salt may be calculated as anhydrous and the difference reported as water of crystallization plus moisture. The latter method is probably the more correct, as it is safe to assume that the crystallized salt has undergone some loss of its water by efflorescence before being incorporated in the explosive mixture.

In either case the algebraic sum of all of the errors in the determinations of the other ingredients of the explosive is thrown on the water when the latter is taken by difference.

In many cases a more correct value for the actual hygroscopic moisture present may be obtained by calculation, assuming certain

average values for the percentage of moisture present in the various ingredients of the mixture.

The average values for the moisture content of the chief ingredients of such explosives, according to the general practice of manufacturers in this country, are approximately as follows:

Approximate average moisture content of constituents of explosives.

	Per cent.
Nitroglycerin.....	0.5
Sodium nitrate.....	.5
Ammonium nitrate.....	.3
Wood pulp.....	5.0
Corn meal.....	12.0
Wheat flour.....	10.0

If these values be assumed to be correct, and the proportion of each constituent of the explosive except moisture has been determined, an approximation to the moisture content of the explosive may be calculated. The following table shows, for a number of explosives of different types made by different manufacturers, a comparison of the calculated moisture content with the result of the determination of moisture by the usual desiccation method, and with that obtained by difference from 100 per cent, as proposed above.

Moisture content of various explosives, as obtained by desiccation, by difference, and by calculation.

Sample No.	Type of explosive.	Moisture content.		
		By desiccation.	By difference.	By calculation.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1	Dynamite (40 per cent strength).....	0.90	0.93
2	do.....	.94	1.00
3	NH ₄ NO ₃ dynamite (40 per cent strength).....	.9275
4	do.....	.9276
5	Permissible explosive (NH ₄ NO ₃ class).....	.4449
6	do.....	.7074
7	Permissible explosive (hydrated class).....	2.10	2.41
8	do.....	2.25	2.24
9	do.....	1.16	1.05
10	do.....20	.41
11	do.....19	.25
12	do.....27	.97
13	do.....	1.00	1.80

For most of the samples the calculated result agrees quite well with the results by desiccation or by difference. The discrepancy of results shown by samples 12 and 13 is probably due to the fact that the crystallized magnesium sulphate in those explosives had partly effloresced, causing the moisture determined by difference to be too low. Cases have been noted where the same cause resulted in a negative value for "moisture by difference." The only feasible manner of reporting the analysis of such explosives is to calculate the crys-

tallized ingredient as anhydrous and estimate by difference the combined moisture and water of crystallization.

EXTRACTION WITH ETHER.

It has been indicated on page 13 that the principal substances that may be found in the ether extracts of permissible explosives are nitroglycerin, nitropolyglycerin, various nitrosubstitution compounds, sulphur, oils, vaseline or paraffin, and resins. Small amounts of oils and resins extracted from the wood pulp or cereal products in permissible explosives are, as in the ordinary types of dynamites, generally found in the ether extract, in addition to materials of similar nature that may constitute actual ingredients of the explosive.

METHOD OF EXTRACTION.

The removal of ether-soluble ingredients from all permissible explosives is carried out according to the general method employed for dynamites.^a Samples of 6 to 10 grams of the explosive in its original condition are weighed in Gooch crucibles with asbestos mats or in suitable porous filtering crucibles, and extracted with ether in a Wiley extractor or other convenient form of reflux-condenser extraction apparatus.

The extraction with ether usually requires about three-quarters of an hour, but it is always advisable to insure that extraction is complete by evaporating a small quantity of the ether passing through the crucible. If the ether completely evaporates, leaving no residue, the extraction is complete.

The crucibles containing the residue insoluble in ether are then removed from the extraction apparatus, the excess of ether in the residue is removed by suction, and the crucibles with their contents are placed at once in a drying oven.

DRYING OF INSOLUBLE RESIDUE.

The method of drying this residue depends upon whether or not the qualitative analysis has shown the presence of ammonium salts or other substances that may be volatilized or decomposed on heating. If the explosive does not contain ammonium salts, it is customary to dry the residue at a temperature of 100° C. for 5 hours, a procedure that has been found to insure constant weight. A longer period of drying, even overnight, will not cause any appreciable additional loss in weight, and is often found convenient.

If ammonium salts are present, the residue is dried at a temperature of 70° C., as it has been shown^b that, especially in the presence

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 30-32.

^b Snelling, W. O., and Storm, C. G., op. cit., pp. 59-60.

of zinc oxide, the antacid generally employed in ammonium nitrate explosives, an appreciable loss of the ammonium salts results from drying at 100° C. At 70° the loss was found to be practically negligible, even on drying for a period of 24 hours.

Organic nitrates, such as nitrostarch or nitrocellulose, may, if present, also undergo some decomposition if the residue is dried as long as 5 hours at 100° C. When the qualitative examination has indicated the presence of either of these substances, it is advisable, therefore, to dry the residue at 70° instead of 100°.

After the drying is completed the crucibles are transferred from the drying oven to sulphuric-acid desiccators, allowed to cool for 15 to 20 minutes, and immediately weighed.

The loss of weight represents the ether-soluble material plus the moisture originally contained in the sample before extraction. If salts containing water of crystallization are a constituent of the explosive, this loss of weight also includes part of the combined water in addition to the free moisture. For example, crystallized magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, if heated sufficiently long at 100° C., loses 5 molecules of its water of crystallization. In the absence of such hydrated salts the total loss obtained by extraction with ether, minus the moisture determined by desiccation, is taken as the amount of ether-soluble material, but when hydrated salts are present the direct weight of residue left on evaporation of the ether solution should be taken as representing the total ether-soluble material.

MODIFIED TUBE FOR WILEY EXTRACTION APPARATUS.

A modified glass tube for use with the Wiley extraction apparatus is shown in figure 4. This form of tube was suggested to the writer by F. B. Stieg, chemist of the Aetna Powder Co., Aetna, Ind., who had devised it for his own use. These tubes are in use in the laboratory of the Bureau of Mines, and are found especially suitable for ether extractions of explosives containing solids, such as trinitrotoluene and sulphur, which are soluble in ether and which crystallize out in the extraction tube during the process of extraction.

When the usual style of extraction tube^a is used it is necessary to transfer the ether extract to small, weighed beakers before evaporating the ether. The presence of crystals in the extract renders this transference more or less troublesome and necessitates the use of an unusual amount of ether for completely removing all of the crystallized material from the tube.

The modified tube shown in figure 4 is approximately the same size as the usual extraction tube, but is made in two parts, the bottom part

^a For description and view, see Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 31, 32.

being $2\frac{1}{2}$ inches deep and $1\frac{1}{4}$ inches inside diameter, and made of glass of such thickness that its weight is approximately 30 grams. The two parts are connected by means of a wide ground joint between the outer surface of the bottom part and the inner surface of the upper part. This ground joint becomes wet with ether during the extraction and is thus rendered perfectly tight.

In using this extraction tube the bottom part is carefully dried and weighed before beginning the extraction. After the extraction is completed the bottom part, containing the ether extract, is removed, placed under the bell-jar evaporator, and the ether evaporated in a current of dry air. The ether-soluble extracted material is then in condition to be weighed, unless the explosive contained a considerable amount of moisture, in which case desiccation is necessary in order to obtain approximately constant weight.

Naturally this style of tube can not be suspended from a ring support, but must be allowed to rest on the top of the heating bath in order to prevent the bottom part of the tube from becoming detached.

EVAPORATION IN THE BELL-JAR EVAPORATOR.

The apparatus used in the bureau's laboratory for evaporating the ether extract is shown in figure 5. It is known as the bell-jar evaporator and was devised by A. L. Hyde, assistant explosives chemist. The beaker, *a*, containing the ether solution is placed on a ground-glass plate, *b*, and covered by a glass bell jar, *c*, 6 inches in diameter and 8 inches high, with tubulures at the top and on the side, each opening being fitted with a perforated stopper and delivery tube. A current of compressed air, dried by passing through con-

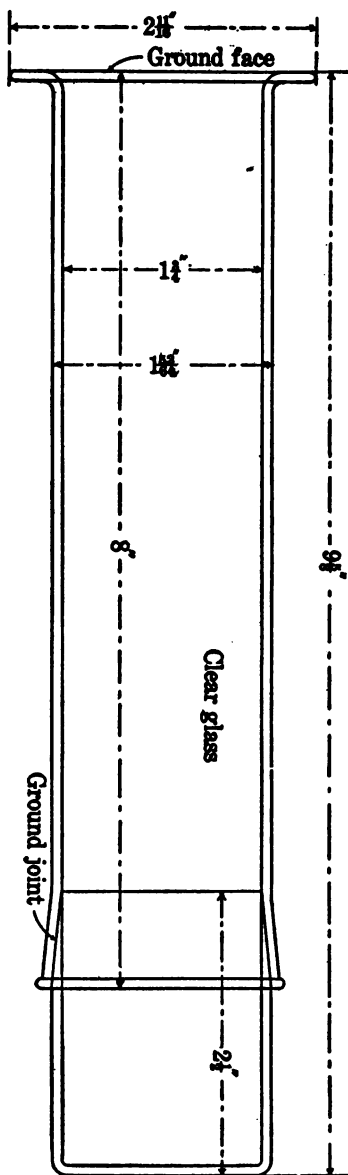


FIGURE 4.—Modified glass tube for use with Wiley extraction apparatus.

centrated sulphuric acid in a drying cylinder, *d*, is passed through the delivery tube in the top of the bell jar, the lower end of the tube being adjusted about one-half inch above the surface of the ether solution in the beaker. A drying cylinder, *e*, filled with granular soda lime is connected between the sulphuric acid cylinder and the bell jar in order to prevent traces of acid from being mechanically carried over. The upper and lower ends of the soda-lime tower are charged with cotton, *f*, which serves as a filter for the air. The air current is so regulated that a marked "dimple" is made in the surface of the solution, care being taken to avoid loss by spattering through using too high an air pressure. The ether vapors pass out through the tube in the side tubulure and may be conducted out of the laboratory.

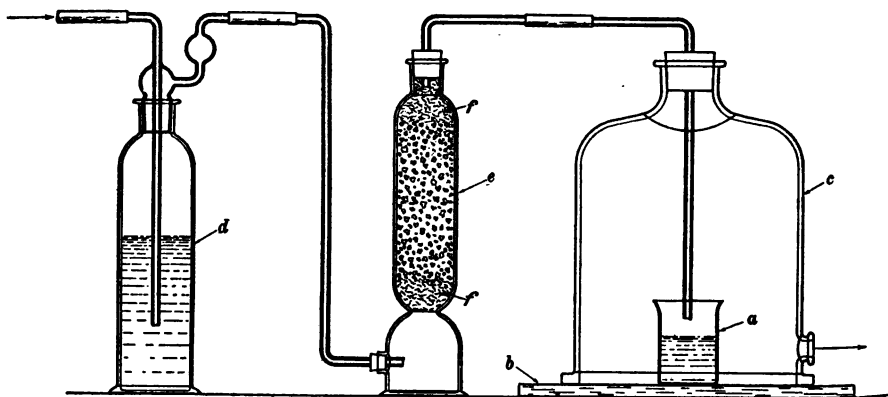


FIGURE 5.—Apparatus for evaporating ether extract.

The advantage in the use of this method of evaporating ether solutions of nitroglycerin lies in the fact that the low temperature produced by the rapid evaporation of the ether minimizes the volatilization of the nitroglycerin and, the air current being dry, there is no deposition of moisture from the air, so that it is only necessary to desiccate the residue, after evaporation of the ether, for a sufficient time to remove the original moisture.

A weighed quantity of nitroglycerin may be dissolved in 50 c. c. of ether and the ether evaporated completely in a few hours with a loss of less than 1 milligram of nitroglycerin, as shown by the nitrometer determinations given on page 38.

ANALYSIS OF ETHER EXTRACT.

The duplicate portions of the ether-soluble material, after all the ether has been removed, as determined by check weighings, are then ready for examination. If qualitative tests have indicated the pres-

ence of nitroglycerin, one of the duplicate samples is used for determining nitroglycerin by means of the nitrometer, as described in Bulletin 51,^a and the other sample is used for the determination of any ingredients other than nitroglycerin. Frequently it is necessary to extract additional samples of the original explosive with ether, in order to obtain a sufficient number of samples of the ether extract for the necessary determinations.

EFFECT OF VOLATILITY OF NITRO COMPOUNDS AND NITROGLYCERIN ON THE RESULTS OF THE ANALYSIS.

The accuracy of the analysis of the ether-soluble part of most permissible explosives is more or less affected by certain properties of substances usually present. For example, nitroglycerin and some of the nitrosubstitution products are appreciably volatile under certain conditions, and in the determination of nitroglycerin by means of the nitrometer some of the other constituents may take up appreciable amounts of the nitric acid liberated from the nitroglycerin, thereby introducing an error in the nitroglycerin determination.

These chief sources of error have been investigated and the results of experiments made are here described.

LOSS OF NITROGLYCERIN DURING EVAPORATION OF THE ETHER SOLUTION.

The subject of loss of nitroglycerin by volatilization has been considered in Bulletin 51,^b where experiments are described showing that spontaneous evaporation of the ether at room temperature results in very slight loss of nitroglycerin. The main objection to this method of evaporation is the fact that an appreciable amount of moisture from the air is deposited with the extract, necessitating desiccation for considerable periods. The use of the bell-jar evaporator described in a preceding paragraph prevents the deposition of moisture. A large number of tests have been carried out to determine the loss of nitroglycerin in evaporating ether extracts with the bell jar.

Weighed samples of nitroglycerin were each dissolved in 50 c. c. of ether in 100-c. c. beakers. The ether was volatilized by subjecting the solution to a current of dry air for a definite length of time in the bell-jar evaporator, then the residue of nitroglycerin, containing possible traces of moisture and ether, was weighed, and the actual proportion of nitroglycerin determined by means of the nitrometer,

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 35-38.

^b Snelling, W. O., and Storm, C. G., op. cit., pp. 39-41.

the use of which is fully described in Bulletin 51.* A number of such determinations are shown in the following table, in which column 1 gives the quantity of nitroglycerin (99.6 per cent pure) taken, column 2 the time of treatment of the ether solution with the air current, columns 3 and 4 the variation of the final weight from the original weight of nitroglycerin, column 5 the quantity of nitroglycerin (calculated to original purity, 99.6 per cent) in the evaporated residue as determined by means of the nitrometer, and column 6 the actual loss of nitroglycerin, or difference between the results in column 1 and column 5.

Loss of nitroglycerin by evaporation of ether solutions by means of dry-air current in bell-jar evaporator.

Test No.	Quantity of nitroglycerin taken for test.	Time of evaporation.	Change in weight.		Quantity of nitroglycerin in residue as determined by nitrometer.	Loss of nitroglycerin.
			Gain.	Loss.		
	1	2	3	4	5	6
	Gram.	Hours.	Gram.	Gram.	Gram.	Gram.
1.....	0.7152	2	0.0033	0.7148	0.0004
2.....	.7025	2	.00017016	.0009
3.....	.7067	3	0.0033	.7037	.0030
4.....	.7091	3	.00047077	.0014
5.....	.7041	30002	.7023	.0018
6.....	.7271	4	.00037263	.0008
7.....	.7014	4	.00057012	.0002
8.....	.7038	40005	.7028	.0010
9.....	.7127	40006	.7105	.0022
10.....	.7260	180005	.7236	.0024
11.....	.7019	180064	.6974	.0045

The results indicate that by evaporating the ether extracts in a dry air current, using the bell-jar evaporator, it is possible to remove practically all of the ether in a few hours without serious loss of nitroglycerin, and without absorption of moisture, obviating the necessity of desiccating the evaporated residue before weighing.

In most of the results cited the weight of the evaporated residue is greater than that of the original sample, owing to some deposition of moisture or to ether residue; in other tests, for example, Nos. 10 and 11, the weight of evaporated residue is less than the weight of 99.6 per cent nitroglycerin calculated from the nitrometer determination, because some of the moisture present in the original nitroglycerin had been evaporated by the long-continued treatment and the purity of the nitroglycerin actually increased thereby. The ether used in these experiments was good quality U. S. P. ether and contained a negligible proportion of nonvolatile residue.

* Snelling, W. O., and Storm, C. G., op. cit., p. 38

EFFECT OF RATE OF AIR CURRENT ON EVAPORATION OF NITROGLYCERIN.

The rate of evaporation and the loss of nitroglycerin for a given period of treatment with the dry air current naturally depend on the rate of the air current. The table following shows the results of two tests in which the samples of nitroglycerin were each dissolved in 50 c. c. of ether and the ether evaporated as above described. A more rapid air current was used to evaporate sample 2, so that in a given period of time the volume of air passed over sample 2 was greater than that passed over sample 1, as indicated by the passage of air through the sulphuric acid in the drying cylinders.

Variation in rate of loss of nitroglycerin by evaporation of ether solutions in dry air current.

Time of evaporation.	Sample 1.			Sample 2.	
	Weight of nitroglycerin.	Change in weight.		Weight of nitroglycerin.	Loss in weight.
		Gain.	Loss.		
Hours.	Grams.	Gram.	Gram.	Gram.	Gram.
0.....	1.2278			0.7019	
3.....	1.2547	0.0269		.7027	a 0.0008
4.....	1.2390	.0112			
5.....	1.2345	.0067		.7018	.0001
6.....	1.2325	.0047		.7016	.0008
7.....	1.2299	.0021		.7007	.0012
8.....	1.2270		0.0008		
9.....	1.2269		.0009	.7002	.0017
10.....	1.2271		.0007	.6999	.0020
11.....	1.2277		.0001	.6996	.0033
12.....	1.2265		.0013	.6976	.0043
13.....	1.2262		.0016	.6973	.0046
14.....	1.2260		.0018	.6968	.0051
15.....	1.2258		.0020	.6966	.0053
16.....	1.2258		.0020		
17.....	1.2257		.0021	.6961	.0058
18.....				.6955	.0064

a Gain.

The results show that a rapid air current removes the ether in a shorter time (3 to 5 hours), but that for long periods of treatment more nitroglycerin is lost than with a slower air current.

It is important that the air current should not be strong enough to cause mechanical loss of the nitroglycerin by spattering.

LOSS OF NITROTOLUENES DURING EVAPORATION OF THE ETHER SOLUTION.

Experiments were also made to determine to what extent the various nitrotoluenes are lost by volatilization during evaporation of the ether from ether solutions containing them. In the tests described below approximately 1 gram of each sample was dissolved in 50 c. c. of U. S. P. ether in a 100 c. c. beaker and the ether evaporated in the bell-jar evaporator, weighings being made at intervals in order to determine any loss of nitro compound.

Results of experiments to determine loss of nitrotoluenes by evaporation of ether solutions with a dry air current in bell-jar evaporator.

Time of evaporation.	Mononitrotoluene (G) (ortho).		Mononitrotoluene (H) (para).		Dinitrotoluene ^a (F) (crystals).		
	Weight of sample.	Loss in weight.	Weight of sample.	Loss in weight.	Weight of sample.	Change in weight.	
						Gain.	Loss.
Hours.	Grams.	Gram.	Grams.	Gram.	Grams.	Gram.	Gram.
0.....	1.0025	1.0072	1.0000
2.....9905	0.0167	1.0285	0.0285
3.....	.9450	0.0575	.9640	.0432	1.0020	.0020
4.....	.9146	.0879	.9375	.0697	1.0009	.0009
5.....	.8850	.1175	.9103	.0969	1.0003	.0003
6.....	.8575	.1450	.8815	.1257	.9995	0.0005
7.....8468	.1604	.99870013
8.....	.8000	.2025	.8397	.1675	.99800020
9.....	.7770	.2255	.8275	.1797	.99760024
10.....	.7450	.2575	.8175	.1897	.99760024
11.....	.7184	.2841	.8047	.2025	.99720028
12.....	.6914	.3111	.7915	.2157	.99670033

Time of evaporation.	Trinitrotoluene ^b (E) (crystals).		Dinitrotoluene (D) (liquid).			Dinitrotoluene (C) (liquid).	
	Weight of sample.	Gain in weight.	Weight of sample.	Change in weight.		Weight of sample.	Loss in weight.
				Gain.	Loss.		
Hours.	Grams.	Gram.	Grams.	Gram.	Gram.	Grams.	Gram.
0.....	1.0000	1.0012	1.0110
2.....	1.0354	0.0342	1.0505	^c 0.0395
3.....	1.0000	0.0000	1.0183	.0171	1.0240	^c .0130
4.....	1.0000	.0000	1.0102	.0080	1.0102	.0008
5.....	1.0000	.0000	1.0082	.0050	1.0030	.0080
6.....	1.0000	.0000	1.0028	.00119959	.0151
7.....9961	0.0051	.9875	.0235
8.....	.9995	^d .0005	.99440083	.9852	.0258
9.....99330079	.9825	.0285
10.....99240083	.9795	.0315
11.....99150097	.9780	.0330
12.....

Time of evaporation.	Trinitrotoluene (B) (liquid).			Trinitrotoluene (A) (liquid).		
	Weight of sample.	Change in weight.		Weight of sample.	Change in weight.	
		Gain.	Loss.		Gain.	Loss.
Hours.	Grams.	Gram.	Gram.	Grams.	Gram.	Gram.
0.....	1.0137	1.0225
2.....
3.....	1.0450	0.0313	1.0650	0.0425
4.....	1.0303	.0166	1.0450	.0225
5.....	1.0250	.0113	1.0355	.0130
6.....	1.0215	.0078	1.0305	.0080
7.....	1.0175	.0038	1.0266	.0041
8.....	1.0130	0.0007	1.0225	.0000
9.....	1.01080029	1.0217	0.0008
10.....	1.00950042	1.02140011
11.....	1.00740063	1.02100015
12.....	1.00610076	1.02000025

^a Melting point 66° to 68° C.

^b Melting point 81° to 82° C.

^c Gain.

^d Loss.

The results are what might be expected from the results of determination of volatility in desiccators, described in pages 24 to 29.

The loss of crystalline trinitrotoluene during evaporation by means of the air current was negligible. The same was true for crystalline dinitrotoluene for periods amply sufficient to remove all ether, although the gradual loss beyond this point indicates that dinitrotoluene is slightly volatile. Both orthomononitrotoluene and paramononitrotoluene volatilized appreciably, even before the evaporation of the ether was complete. The evaporation of the ether from the "liquid dinitrotoluenes" and "liquid trinitrotoluenes" apparently proceeded more slowly than from the crystalline compounds, 5 to 8 hours' treatment being necessary before the liquid samples attained approximately their original weight.

On further treatment with the air current the "liquid trinitrotoluenes" underwent a slight loss of weight and the "liquid dinitrotoluenes" a somewhat greater loss. In general, it is noted that the loss of weight is greater as the percentage of mononitrotoluene is greater.

CONCLUSIONS REGARDING LOSS BY EVAPORATION OF THE ETHER EXTRACT.

The experiments indicate that by the use of the bell-jar evaporator, with a fairly rapid current of dry air, ether solutions may be evaporated in about 5 to 6 hours without an appreciable loss of either nitroglycerin or nitrotoluenes, provided that no great proportion of mononitrotoluene is present. Seven to eight hours may be necessary for complete removal of the ether from "liquid trinitrotoluene," and even an 8-hour treatment will not cause any appreciable loss of nitroglycerin.

EFFECT OF VARIOUS SUBSTANCES ON THE DETERMINATION OF NITROGLYCERIN BY MEANS OF THE NITROMETER.

It has been shown* that mononitrotoluene, which is usually a constituent, in greater or less proportion, of most of the commercial "liquid nitrotoluenes" used in blasting explosives, interferes with the direct determination of nitroglycerin by means of the nitrometer. Other mononitro compounds affect the determination in the same manner, by combining with part of the nitric acid resulting from the breaking up of the nitroglycerin. Certain substances other than nitrosubstitution compounds, which may be found in the ether extracts of explosives, have the same effect. A series of experiments were made in order to determine the extent to which the determination of nitroglycerin in the nitrometer is affected by the presence of such substances as may be contained with the nitroglycerin in the ether extract.

* Storm, C. G., Effect of nitrotoluenes on the determination of nitroglycerin by means of the nitrometer: Original Communications, 8th Int. Cong. App. Chem., vol. 4, 1912, p. 117.

TESTS OF ETHER-SOLUBLE SUBSTANCES.

The substances used in these tests included the more common nitro-substitution compounds, rosin (colophony), vaseline, paraffin, and various mineral and vegetable oils. A weighed quantity of the material to be tested was placed in a small beaker, a weighed quantity of either nitroglycerin or potassium nitrate of known nitrogen content (18.46 and 13.84 per cent, respectively) added, and the whole treated with about 10 c. c. of strong sulphuric acid, approximately 96 per cent pure. The mixture was well stirred with a small glass rod and transferred to the generating bulb of the nitrometer, fresh sulphuric acid being used to completely remove any undissolved material left in the beaker. In most of the tests 20 to 30 c. c. of sulphuric acid was sufficient. After shaking the mixture in the generator until the evolution of nitric oxide (NO) was complete, the gas was transferred to the reading tube and the volume read. This reading is expressed in terms of weight of nitrogen found (grams) in column 4 of the following table of results. The figures given in column 5 for the weight of nitrogen lost per gram of ingredient (column 3) are obtained by deducting the weight of nitrogen found (column 4) from the weight of nitrogen present (weight of KNO_3 , times $\frac{13.84}{100}$, or weight of nitroglycerin times $\frac{18.46}{100}$), and dividing the remainder by the weight of substance as given in column 3. Column 5 also shows the equivalent of the nitrogen loss in terms of nitroglycerin; or, in other words, the loss of nitroglycerin which would result from the presence of 1 gram of the substance indicated in column 3.

Results of determinations of nitrogen in the nitrometer in the presence of various ether-soluble substances.

VASELINE.

Weights of ingredients of mixture.			Results of determination.			
KNO_3 .	Nitroglycerin.	Substance tested.	Weight of N found.	Weight of N lost per gram of substance tested.	Average loss of N per gram of substance tested.	Equivalent loss of nitroglycerin per gram of substance tested.
1	2	3	4	5	6	7
Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
1.0000	0.4006	0.1302	0.0205	} 0.0218	0.1180
1.00002052	.1335	.0239		
1.00001046	.1364	.0191		
.....	0.7192	.2010	.1281	.0239		

Results of determinations of nitrogen in the nitrometer in the presence of various ether-soluble substances—Continued.

PARAFFIN.

Weights of ingredients of mixture.			Results of determination.			
KNO ₃ .	Nitroglycerin.	Substance tested.	Weight of N found.	Weight of N lost per gram of substance tested.	Average loss of N per gram of substance tested.	Equivalent loss of nitroglycerin per gram of substance tested.
1	2	3	4	5	6	7
Gram. 1.0000	Gram. 0.7624	Gram. 0.1670 .1012	Gram. 0.1358 .1391	Gram. 0.0155 .0158	Gram. 0.0157	Gram. 0.0849

CASTOR OIL.

1.2000	0.8491	0.1688 .1557	0.1564 .1475	0.0575 .0591	0.0583	0.3151
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COTTONSEED OIL.

1.0000	0.4229 .2311	0.1025 .1187	0.0849 .0852	0.0851	0.4589
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ENGINE OIL.

1.0000	0.1050 .3192 .1592	0.1334 .1229 .1294	0.0476 .0485 .0484	0.0482	0.2605
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CORN OIL.

1.0000	0.1054 .2044	0.1316 .1430	0.0645 .0800	0.0623	0.3368
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ROSIN (COLOPHONY).

(10) 191000

0.7552 .7394 .7590	0.1006 .1008 .2017	0.1316 .1289 .1248	0.0775 .0744 .0758	0.0759	0.4103
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MONONITRONAPHTHALENE.

1.0000	0.1000 .2012 .3000 .1006 .1527 .2520	0.1219 .1061 .0894 .1219 .1140 .1045	0.1650 .1605 .1633 .1640 .1598 .1600	0.1621	0.8762
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MONONITROBENZENE.

1.3190 1.3053	1.0017 .9981	0.1276 .1259	0.1157 .1152	0.1155	0.6243
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DINITROBENZENE.

1.0000	0.1966 .9993	0.1384 .1311	0.0000 .0007	0.0000 .0007	
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DISCUSSION OF RESULTS OF TESTS.

The above results show that such materials as rosin, vaseline, paraffin, and mineral and vegetable oils are all capable of being nitrated, and hence take up part of the nitric acid liberated from the nitroglycerin by the reaction in the nitrometer. Furthermore, the proportion of nitrogen thus combined by such materials is practically a constant quantity for each gram of the material, regardless of the quantity present.

All mononitro compounds are probably capable of becoming further nitrated under the conditions existing in the nitrometer, and the tests made indicate that in each instance the mononitro compound is nitrated to a definite degree, taking up either one or two more nitro groups. The previous work of the writer,^a referred to in a preceding paragraph, showed that the mononitrotoluenes are quantitatively converted to dinitrotoluenes but that dinitrotoluenes and trinitrotoluenes are not acted on in the nitrometer. The results in the table show analogous action of mononitrobenzene and dinitrobenzene; 1 gram of mononitrobenzene absorbed 0.1152 gram nitrogen, whereas for conversion to dinitrobenzene it should absorb 0.1138 gram. Dinitrobenzene was practically without effect on the determination. Mononitronaphthalene, however, was converted by the reaction in the nitrometer to trinitronaphthalene, 1 gram of the mono compound taking up 0.1621 gram of nitrogen, whereas the quantity theoretically required for the conversion to trinitronaphthalene is 0.1597 gram.

This conclusion was confirmed by the following experiment: 2 grams of mononitronaphthalene was added to 2.4 grams potassium nitrate and the mixture treated in a beaker with about 25 c. c. of 96 per cent sulphuric acid, stirred, and let stand for 2 hours until cooled to room temperature. The mixture was then poured into 500 c. c. water, the resulting precipitate filtered off, washed, and dried to constant weight in a vacuum desiccator. The product weighed 2.94 grams, whereas if the mono compound had been completely converted to trinitronaphthalene the weight should have been 3.04 grams. The original mononitronaphthalene, which theoretically contained 8.09 per cent nitrogen, was found to contain 8.16 per cent nitrogen, and the product obtained by the above reaction contained 15.67 per cent nitrogen, whereas trinitronaphthalene theoretically contains 15.97 per cent of nitrogen.

The interference of ether-soluble substances with the determination of the nitroglycerin may be avoided if any substances in the ether extract other than nitroglycerin are determined by a direct method and the nitroglycerin determined by difference. The direct

^a Storm, C. G., Effect of nitrotoluenes on the determination of nitroglycerin by means of the nitrometer: Original Communications; 8th Int. Cong. App. Chem., vol. 4, 1912, p. 117.

determination of these ether-soluble materials is discussed in pages 46 and 47.

TESTS TO ASCERTAIN SOLUBILITY OF ETHER-SOLUBLE SUBSTANCES IN NITROGLYCERIN.

A series of tests was made to ascertain the extent to which the solubility of these ether-soluble substances in the nitroglycerin would affect the determination of the purity of the nitroglycerin separated from such substances by filtration. About 0.5 gram of the substance taken for test was added to 2 c. c. of nitroglycerin of known nitrogen content (18.42 per cent), the whole dissolved in 50 c. c. of ether, the ether evaporated by the method described for treating the ether extract of an explosive (pp. 35 and 36), the evaporated material filtered through a paper filter, and the clear filtrate tested in the nitrometer. From the result of the nitrogen determination it is readily ascertained whether an appreciable quantity of the substance has been dissolved by the nitroglycerin. For example, a determination giving a nitrogen content of 18.32 per cent indicates that 1 per cent of the substance is dissolved in the filtered nitroglycerin; 18.13 per cent N indicates that 2 per cent of the substance has been dissolved, and so on, provided that any nitrogen taken up by the dissolved material is disregarded.

The table following shows the results of the tests made:

Results of tests to determine nitrogen content in nitroglycerin filtered from various ether-soluble substances.

Substance with which nitroglycerin was mixed.	Nitrogen content of filtered nitroglycerin.	Substance with which nitroglycerin was mixed.	Nitrogen content of filtered nitroglycerin.
	<i>Per cent.</i>		<i>Per cent.</i>
Vaseline, refined.....	18.42 to 18.37	Engine oil.....	18.16
Vaseline, crude.....	18.39 to 18.37	Corn oil.....	18.35
Paraffin.....	18.42 to 18.43	Mononitronaphthalene.....	13.44
Sulphur.....	18.07 to 18.05	Mononitrotoluene (para).....	14.94
Rosin (colophony).....	18.43 to 18.44	Dinitrotoluene (crystals) ^a	15.60
Castor oil.....		Trinitrotoluene (crystals) ^b	15.43
Cottonseed oil.....		Resins extracted from wood pulp:	
		Sample 1.....	17.96
		Sample 2.....	17.78
		Sample 3.....	17.77
		Oil extracted from corn meal.....	18.42
		Oil extracted from wheat middlings.....	18.43

^a Melting point, 66° to 68° C.

^b Melting point, 81° to 82° C.

The above results show that vaseline, paraffin, sulphur, cottonseed oil, castor oil, corn oil, and wheat oil are practically insoluble in nitroglycerin, and that the nitroglycerin mixed with them may be obtained in sufficient purity, for identification and test, by filtering through a paper filter, as the oily materials remain on the filter.

Ordinary commercial rosin (colophony), and the resinous material obtained by extracting wood pulp with ether, and engine oil, and

crystalline nitrosubstitution compounds, including mononitronaphthalene, mononitrotoluene, dinitrotoluene, and trinitrotoluene, are all soluble in nitroglycerin to an extent that vitiates the determination of nitrogen in the filtered nitroglycerin. For this reason the nitroglycerin obtained, by extraction with ether, from explosives containing wood pulp shows a slightly low figure for nitrogen content, even when the small proportion of resinous substances is removed by filtering.

DETERMINATION OF SULPHUR IN THE ETHER EXTRACT.

If an explosive contains sulphur, some of the sulphur will be found in the ether extract. However, as sulphur is only slightly soluble in ether, it is advisable to make an additional extraction with carbon bisulphide, preferably after extracting with water, in order to insure complete removal of the sulphur.

If crystals of sulphur are noted in the ether extract, the procedure is usually as follows:

The extract from which all ether has been evaporated is poured from the beaker into a dry paper filter fitted in a small funnel, and the clear liquid (generally nitroglycerin) allowed to filter through into a small weighed beaker. A convenient amount (approximately 0.7 gram) of this filtrate is used for a determination in the nitrometer to ascertain whether it is pure nitroglycerin or contains other liquid or dissolved ingredients. A nitrogen content of 18.30 per cent or more, indicating at least 99 per cent of nitroglycerin, may be considered as denoting freedom from any other liquid or dissolved material in appreciable quantities.

The nitroglycerin left in the filter is completely removed by washing with 70 per cent acetic acid, leaving the sulphur on the filter. Any sulphur in the beaker that originally contained the extract is also transferred to the filter by washing with acetic acid. The sulphur is then freed from acetic acid by washing with water, dried, and weighed. To the quantity of sulphur thus found is added the quantity found later by extraction with carbon bisulphide.

DETERMINATION OF VASELINE, PARAFFIN, OILS, AND RESINS IN THE ETHER EXTRACT.

Vaseline, paraffin, oils, and similar substances in the ether extract may be separated from the nitroglycerin by the method that is used for separating the sulphur, namely, by dissolving the nitroglycerin, nitrotoluene, etc., in acetic acid (70 per cent pure) and collecting the insoluble substances on a paper filter, from which they may be again dissolved by means of ether, the ether removed by evaporation, and the oily material weighed. The sulphur, if any, will be left on the

filter, together with the vaseline, paraffin, or oil, in which case the oily substances may be extracted from the sulphur with a small quantity of ether or petroleum ether, in both of which sulphur is only slightly soluble, the solvent evaporated, and the oily substance weighed.

Resin, if present, will be dissolved by the acetic acid used for removing the nitroglycerin and should be determined in a separate part of the ether extract by titration with a saturated solution of alcoholic potash^a or by saponifying the nitroglycerin with alcoholic potash, acidifying, and weighing the separated resin.^b

DETERMINATION OF NITROSUBSTITUTION COMPOUNDS IN THE PRESENCE OF NITROGLYCERIN.

A satisfactory method for the separation of nitrosubstitution compounds from nitroglycerin has been worked out in the explosives chemical laboratory of the Bureau of Mines by A. L. Hyde,^b assistant chemist.

This method depends on the differences in solubility of nitroglycerin and nitrosubstitution compounds in carbon bisulphide and mixtures of acetic acid and water. Nitroglycerin is only slightly soluble in carbon bisulphide, but is readily soluble in mixtures of acetic acid and water, whereas most of the nitro compounds, although not readily soluble in carbon bisulphide, are more soluble in it than nitroglycerin and are less soluble than nitroglycerin in mixtures of acetic acid and water. Carbon bisulphide and mixtures of acetic acid and water are only slightly miscible. Hence nitroglycerin and a nitro compound may be partly separated by shaking the mixture with carbon bisulphide and a solution of acetic acid and water, allowing the two solvents to separate into two layers and drawing off one of the layers. The carbon-bisulphide layer will contain the greater proportion of nitrosubstitution compound and the acetic-acid layer the greater proportion of nitroglycerin.

The method devised by Hyde involves a continuous fractional separation of the ingredients of such mixtures. The following description of the apparatus and method, as in use in the explosives laboratory of the bureau, is taken from Hyde's paper.^c

DESCRIPTION OF APPARATUS.

The apparatus consists of a series of 13 tubes for holding the 2 solvents, a circulating system made of glass tubing, a flask, which may be heated in any convenient manner, at one end of the system, a return pipe from this flask, and a measuring device, condenser, and reservoir at the other end of the system.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 41-42.

^b Hyde, A. L., The quantitative separation of nitrosubstitution compounds from nitroglycerin: Jour. Am. Chem. Soc., vol. 35, September, 1913, p. 1173.

^c Hyde, A. L., loc. cit.

The whole is mounted in a wooden frame of suitable form and size, as shown in figure 6.

The tubes for holding the solvents are made in the form shown. The main shank has an inside diameter slightly less than 1 cm. and a length of about 19 cm. The top and bottom parts have an inside diameter of about 2 cm. The bottom part is about 4 cm. long, the top part about 6 cm. The top of each tube is closed with a No. 3 two-hole rubber stopper.

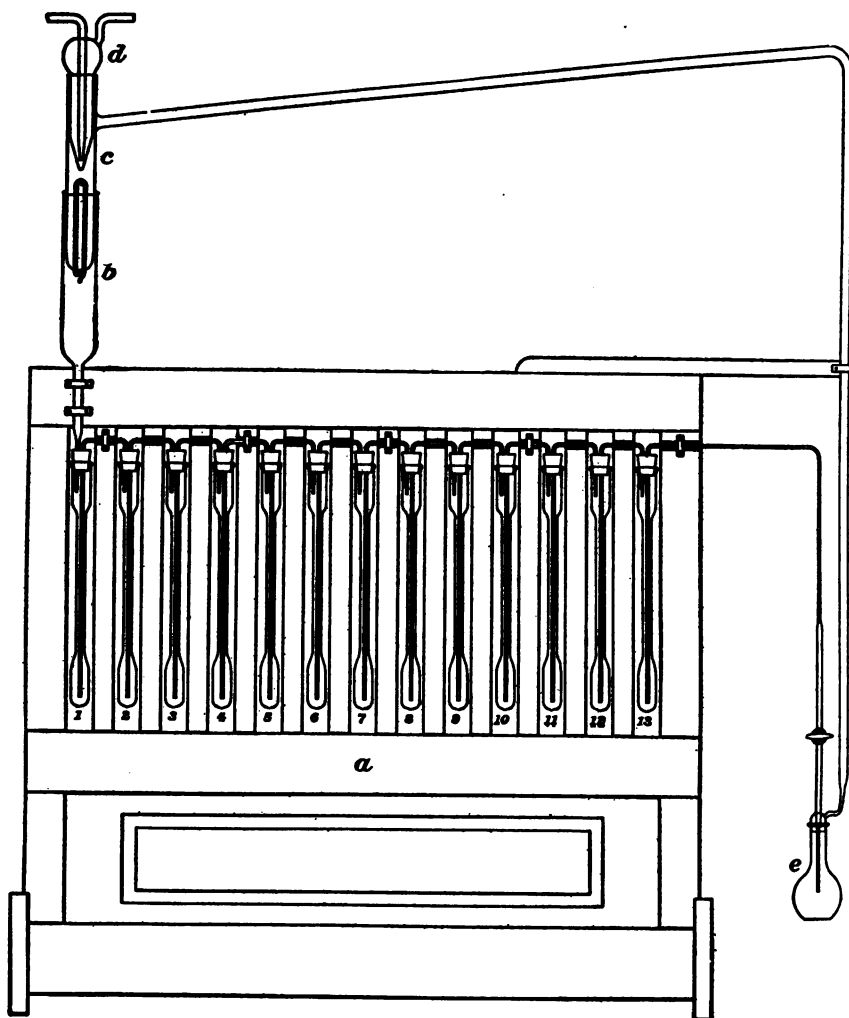


FIGURE 6.—Apparatus for separation of nitrosubstitution compounds from nitroglycerin. *a*, Support; *b*, reservoir; *c*, condenser; *d*, measuring device; *e*, collecting flask; 1 to 13, tubes.

The circulating system consists of a series of glass tubes of a size to fit snugly the holes of the No. 3 stoppers, and bent at the top in the form of an inverted U. The long arm of each tube is long enough, when passed through the No. 3 stopper and the stopper is tightly inserted in the reaction tube, to reach almost to the bottom of the reaction tube. The short arm, about 6 cm.

long, is drawn to capillary size at the end. The long arm of each tube is passed through one hole of a rubber stopper and the short arm through a hole of the stopper next in the series so that the tubes form a continuous chain. A tube leading from the reservoir passes through the first stopper of the series, and a tube leading from the bottom of the last reaction tube to the collecting flask passes through the last stopper.

The bottom of the collecting flask is situated about 30 cm. lower than the bottom of the reaction tubes in order that a siphon may be formed to cause a continuous flow of liquid through the tubes into the flask. Just above the flask is a stopcock designed to regulate the flow through the siphon. The flask has a ground-glass stopper with two openings, one of which is connected with the return pipe to the condenser.

The condenser is provided with a siphon measuring device, holding 80 c. c., for measuring the quantity of solvent that passes through the system. This measuring device empties directly into the reservoir below. The whole circulating system is fastened in the wooden stand and remains there permanently, but the reaction tubes may be removed for cleaning and filling. When the reaction tubes are filled and in place the whole series forms an air-tight system.

OPERATION OF THE APPARATUS.

To use the apparatus, tubes 2 to 11, inclusive, are filled up to the bottom of the shank with carbon bisulphide, and the remainder of their length with a mixture consisting of 75 per cent acetic acid and 25 per cent water. About 170 c. c. of the mixture are required for the entire apparatus. The mixture should nearly touch the stopper when the tube is placed in the system, thus allowing the capillary point of the U-tube to dip 2 or 3 cm. into the liquid. Tubes 12 and 13 are filled in the same way, but with water instead of acetic-acid mixture, and are intended to take up any small quantities of acetic acid carried along with the carbon bisulphide from the other tubes. Except for this precaution considerable acetic acid would be carried into the collecting flask and cause delay in subsequent evaporation.

After the solvent tubes are in place the mixture to be separated is dissolved in 10 to 15 c. c. of a mixture of acetic acid and water, and the solution is poured into tube 1 on top of the layer of carbon bisulphide already poured into the bottom part of the tube. When tube 1 is in place carbon bisulphide is poured into the measuring device until it runs over into the reservoir, the collecting flask is put in place, and the process is started by opening the cock just above the collecting flask. The rate of flow is regulated by means of the cock so that 3 to 4 c. c. of solvent flows into the flask per minute. The flask is heated by immersing it in a dish of hot water, which is heated by a small electric heater.

The action that takes place is as follows: Carbon bisulphide coming down through the tube from the reservoir falls in fine drops through the acetic-acid solution containing both nitroglycerin and the nitro compound, extracts some of both, and carries this over into tube 2. Here the carbon bisulphide again falls through the acetic-acid mixture in a series of fine drops, and most of the nitroglycerin and some of the nitro compound are extracted. The same process is repeated in each reaction tube, the solvent stream being freed more and more from nitroglycerin as it progresses along the system. After a certain quantity of carbon bisulphide has passed through the system, nitro compound, entirely free from nitroglycerin, begins to appear in the stream flowing into the collecting flask. If sufficient solvent is passed through the system, prac-

tically all of the nitro compound will be carried over into the collecting flask. While the solvent is flowing into the collecting flask it is also being evaporated and passed back to the condenser to be used again. After the process is completed the flask is removed, the solution poured into a small beaker, the solvent evaporated in a bell-jar evaporator,* and the nitro compound weighed.

In the case of a nitro compound much more soluble in carbon bisulphide than nitroglycerin is, practically all the nitro compound will have passed into the collecting flask before traces of nitroglycerin appear there. In case, however, the difference in solubility is slight, small quantities of nitroglycerin will begin to appear in the collecting flask before all the nitro compound has come over. It is obvious that in these cases a perfectly sharp quantitative separation can not be made with a single fractionation, but even in these cases, as will be shown, it is possible to obtain satisfactory results with a single fractionation by regulating the quantity of solvent passing through the system.

It is evident that with a nitro compound whose solubility is only slightly different from that of nitroglycerin, the accuracy of the separation depends upon stopping the process after most of the nitro compound has passed over and before much nitroglycerin begins to pass over.

It was found that the passage of about 880 c. c. of carbon bisulphide through the apparatus sufficed to carry over practically all the nitro compound. Three mixtures were tested using this quantity of solvent. The results are noted below:

Results of separation of nitrotoluenes from nitroglycerin.

Mixture.	Components.	Composition of mixture.			
		Actual.		By analysis.	
		Grams.	Per cent.	Grams.	Per cent.
1	Nitroglycerin.....	2.623	52.7	2.595	52.2
	"Liquid trinitrotoluene".....	2.353	47.3	2.381	47.8
2	Nitroglycerin.....	2.838	63.5	2.831	63.4
	"Liquid trinitrotoluene".....	1.631	36.5	1.638	36.6
3	Nitroglycerin.....	3.400	78.1	3.406	78.2
	"Liquid trinitrotoluene".....	.955	21.9	.949	21.8

In order to determine whether any nitroglycerin was present in the product obtained in the collecting flask, tests were made in several of the foregoing experiments. These tests showed that in no case was the separation entirely complete, but that 1 to 2 per cent of the quantity of nitroglycerin originally present had passed into the collecting flask. However, as the above results show, the accuracy is sufficient for most purposes. If in any particular case it is desired to obtain the nitro compound more nearly free from nitroglycerin than can be obtained with one separation, a second separation may be made, which will still further reduce the proportion of nitroglycerin. But this is a rather tedious process and usually should not be necessary. A double separation of one mixture was made to determine what accuracy could be expected.

The mixture contained 3.475 grams, or 58.8 per cent of nitroglycerin, and 2.434 grams, or 41.2 per cent of liquid trinitrotoluene. The nitrotoluene obtained after two separations weighed 2.388 grams, or 40.4 per cent of the original mixture. A test of the nitrotoluene separated showed that it contained less than 10 mg. of nitroglycerin.

* For description of evaporator see pp. 35 and 36 of this bulletin.

Additional experiments showed that certain other nitrosubstitution compounds besides the nitrotoluenes could be readily separated from nitroglycerin by this method; for example, mononitrobenzene, dinitrobenzene, and mononitronaphthalene, and, further, that various nitrosubstitution compounds may be just as readily separated from each other, the only requirement being that there shall be sufficient difference in their solubilities.

It is likely that, by slight changes in the solvents (for example, in the strength of the acetic acid), the method may be applied to the separation of any nitrosubstitution compounds from nitroglycerin or from each other, and even to the separation of oils and other ether-soluble materials from nitroglycerin, etc.

DETERMINATION OF NITROPOLYGLYCERIN IN MIXTURE WITH NITROGLYCERIN.

Some types of low-freezing explosives contain mixtures of nitroglycerin and nitropolyglycerin, the effect of the latter being to greatly reduce the freezing point of the nitroglycerin. This mixture is usually prepared as follows: Glycerin is polymerized by one of the usual methods, generally at an elevated temperature and high pressure. The resulting product is a mixture of polymerized glycerin and unaltered glycerin, varying in composition according to the length and conditions of treatment. It is probable that the polymerized glycerin contains small amounts of polymers higher than diglycerin.

This product is then nitrated in the same manner as ordinary glycerin, the nitrated material consisting of a mixture of trinitroglycerin, tetranitrodiglycerin and corresponding nitrates of whatever higher polymers may be present.

This mixture is in appearance and general properties similar to ordinary nitroglycerin, and in a hasty analysis might be mistaken for it. The best means of identifying the nitropolyglycerin are by (1) determination of nitrogen content, (2) determination of molecular weight, and (3) determination of solubility. For all of these determinations the residue left after evaporation of the ether from the ether extract should be filtered in order to remove resins, sulphur, or other substances which form a sort of scum on the surface of the liquid. A small filter paper in a small funnel can be used for the filtration and a clear liquid is easily obtained.

METHOD FOR DETERMINING THE NITROGEN CONTENT OF THE MIXTURE.

In determining the nitrogen content of a mixture of nitroglycerin and nitropolyglycerin by means of the nitrometer about 0.75 gram of the filtered ether extract is used for the determination. The nitrogen content of pure nitroglycerin being 18.5 per cent and that of

tetranitrodiglycerin 16.19 per cent, the approximate proportions of these two compounds in the mixture are readily calculated (any small content of higher polymers being disregarded).

BOILING-POINT METHOD FOR DETERMINING MOLECULAR WEIGHT OF THE MIXTURE.

For determining the molecular weight of a mixture of nitroglycerin and nitropolyglycerin the boiling-point method has been found to give satisfactory results, ethyl acetate being used as a solvent.*

The apparatus used for this purpose in the bureau's laboratory is a slight modification of the well-known Beckmann apparatus. The solution is heated internally by means of an electric heating coil of fine platinum wire sealed into the bottom of the tube, and in order to minimize the change in concentration of the solution a condensing coil of copper tubing is wrapped around the outside of the tube just above the surface of the solution. Circulation of cold water through this coil keeps the walls of the boiling tube cold and provides for quick condensation of the vapors of the solvent. The thermometer used is an ordinary Beckmann differential thermometer, reading to hundredths of a degree.

The method used is as follows: About 12 c. c. of pure ethyl acetate is placed in the tube, the thermometer inserted, and the solvent boiled until equilibrium is established. The boiling point is then noted and the tube is emptied and dried. A weighed quantity of the mixture to be tested (2.5 to 3 grams) is dissolved in about 10 c. c. of the ethyl acetate, the solution is then weighed and quickly transferred to the boiling-point tube. The boiling point of the solution is determined under the same conditions as that of the pure solvent; the difference in the boiling points represents the effect of the dissolved material.

Assuming that the law for dilute solutions holds also in the case of more concentrated solutions, the molecular weight of the substance is $m = \frac{gr}{a}$, where g is the weight in grams of added substance per 100 grams of solvent, a the rise in boiling point, and r the boiling-point constant of the solvent used ($r = 26.1$ for ethyl acetate^b).

It has been shown by Hyde^c that excellent results may be obtained with this method if ethyl acetate be used as the solvent, but that results with ether, acetone, methyl alcohol, and chloroform are not concordant and vary rather widely with the concentration of the solution. Many determinations on pure nitroglycerin by this method have given for the molecular weight values ranging from 229 to 235. The theoretical molecular weight is 227.

* Hyde, A. L., Boiling points of solutions of nitroglycerin: Original Communications, 8th Int. Cong. App. Chem., vol. 4, 1912, p. 59.

^b Biedemann, R., Chemiker Kalender, 1910, vol. 2, p. 49.

^c Hyde, A. L., loc. cit.

THE TWO METHODS COMPARED.

In order to test the value of this method in comparison with the nitrometer method, a sample of partly polymerized glycerin was nitrated and washed free from acid. The resulting mixture of nitroglycerin and nitropolyglycerin was found by test in the nitrometer to contain 16.85 to 16.88 per cent of nitrogen. Assuming the mixture to consist of nitroglycerin (18.50 per cent nitrogen) and tetranitrodiglycerin (16.19 per cent nitrogen), the nitrogen content of the mixture corresponds to that of a mixture containing 29.23 per cent nitroglycerin and 70.77 per cent tetranitrodiglycerin. Such a mixture would have a molecular weight (calculated) of 311. The molecular-weight determination made as above described gave results of 306 and 314, an average of 310.

A second sample of partly polymerized glycerin was nitrated in a similar manner and the nitrated product tested, with the following results:

The nitrogen content was 16.58 to 16.63 (average 16.605) per cent, corresponding to a mixture consisting of 17.75 per cent nitroglycerin and 82.25 per cent tetranitrodiglycerin. The calculated molecular weight of this mixture is 325; the molecular weight as determined was 325 and 328, the average being 326.5.

In both tests the results of the determinations of nitrogen and molecular weight agree very closely.

METHOD FOR DETERMINING SOLUBILITY OF THE MIXTURE.

The difference in solubility of nitroglycerin and nitropolyglycerin in dilute acetic acid (60 volumes of glacial acetic acid to 40 volumes of water) provides a convenient means of identifying nitropolyglycerin in such a mixture.

Experiments have shown that 1 gram of nitroglycerin will completely dissolve in approximately 10.5 c. c. of dilute acetic acid of the concentration mentioned—the specific gravity of such a mixture is approximately 1.069 at 15° C.—whereas nitropolyglycerin is much less soluble. One gram of the mixture of nitroglycerin and nitropolyglycerin previously mentioned containing 82.25 per cent tetranitrodiglycerin required 120 c. c. of the acetic-acid solution to completely dissolve it. In treating this sample with the acetic acid, adding the acid in small quantities and shaking thoroughly after each addition, it was found that when about 50 c. c. had been added only a small quantity of the mixture remained undissolved, and this small quantity required about 70 c. c. more acid for complete solution, the volume of the undissolved part decreasing slightly with each addition of 10 c. c. of acid.

Although no definite conclusions as to the presence of nitropolyglycerin should be made from the results of any one of the three

tests described, it is apparent that the data supplied by all three tests when combined is sufficient to determine whether there is any nitropolyglycerin in the ether extract.

This point may be illustrated by the following description of an actual analysis. The ether extract from an ammonium-nitrate explosive was an oily liquid with the appearance of nitroglycerin. A filtered part of this extract was found by the nitrometer to contain only 17.7 per cent nitrogen. A molecular-weight determination on another part gave a result of 265, indicating a mixture with a molecular weight greater than that of nitroglycerin. About 5 grams of the extract was shaken with 150 c. c. of 60 per cent acetic acid (nearly three times the amount necessary to dissolve 5 grams of pure nitroglycerin). The insoluble part was separated, washed, dried, and its nitrogen content, determined in the nitrometer, was 16.24 per cent, which is almost the theoretical nitrogen content (16.19 per cent) of tetranitrodiglycerin.

If the extract is composed of nitroglycerin and tetranitrodiglycerin, the nitrogen content of 17.7 per cent indicates a mixture consisting of 65.4 per cent nitroglycerin and 34.6 per cent tetranitrodiglycerin, whereas the molecular weight 265 indicates a mixture containing 68 per cent nitroglycerin and 32 per cent tetranitrodiglycerin. It is therefore safe to assume that the extract consists of approximately 2 parts of nitroglycerin to 1 part of tetranitrodiglycerin.

EXTRACTION WITH WATER.

METHOD OF EXTRACTING WATER-SOLUBLE INGREDIENTS.

In practically all types of permissible explosives the extraction with water is carried out on the dried and weighed residues left in the extraction crucibles after extracting with ether. The method employed is the same as in the treatment of ordinary dynamites.* The Gooch crucible is inserted in the top of a carbon filter tube, which is fitted with a short length of thin-walled rubber tubing to make a tight joint between the crucible and the filter tube. The lower end of the filter tube is passed through a rubber stopper in the mouth of a side-neck suction flask. About 200 c. c. of cold distilled water is then passed through the sample in each crucible in quantities of about 20 c. c. each, each addition of water being allowed to stand in the crucible for a short time before it is drawn into the flask. The necessary suction is obtained from an ordinary filter pump operated by water pressure. A few drops of the last addition of water passed through the sample are tested by evaporation on a glass plate to insure that all water-soluble material has been dissolved.

* See Snelling, W. O., and Storm, C. G., *The analysis of black powder and dynamite*: Bull. 51, Bureau of Mines, 1913, p. 43.

If the qualitative analysis of the explosive has indicated that it contains a considerable proportion of starch, the extractions will be facilitated by the use of porous alundum filtering crucibles in place of the ordinary porcelain Gooch crucibles, as the porous crucibles permit the water solution to filter through the walls of the crucible above the dense layer of starch which will separate out in the bottom of the crucible. With porous crucibles, however, it has been found advisable to use the Spencer glass funnel,^a which provides for a tight joint between the top of the crucible and the walls of the funnel by means of a soft rubber ring resting on top of the crucible. By means of this apparatus the absorption of water-soluble salts in the upper part of the wall of the crucible is avoided, as the crucible may be entirely filled with each addition of water, completely removing all soluble material. Perfect washing of the upper part of the porous crucibles is practically impossible when the ordinary carbon filter tubes are used.

Another device which has been found to insure complete removal of the water-soluble material from the porous crucibles is the so-called "filtering crucible holder," which enables the porous crucible to be used with any ordinary 60-degree funnel. The holder consists of a hard-rubber device with a soft flange forming tight joints with the walls of the funnel on one side and with the extreme top of the crucible walls on the other side. Both of the above devices are used in the explosives laboratory of the Bureau of Mines and give satisfactory results.

The water extracts are transferred from the suction flasks, diluted with distilled water to a known volume, usually 250 c. c. each, and reserved in stoppered bottles for quantitative determination of the dissolved ingredients.

DRYING OF INSOLUBLE RESIDUE.

The crucibles, after the contents have been subjected to extraction with water, are placed in a drying oven and the residue dried to constant weight. About five hours' drying at a temperature of 95° to 100° C. is usually necessary for thorough drying of the residue, especially if it contains wood pulp, cereal products, or other organic materials, and it is often convenient to continue the drying for a longer period, for example, overnight. Upon removal from the oven the crucibles with their contents are placed in a tight desiccator, preferably over sulphuric acid, and weighed as soon as they have cooled to room temperature, about 15 to 20 minutes being sufficient for cooling.

^a Spencer, G. L., Alundum crucibles in gravimetric analyses: Jour. Ind. Eng. Chem., vol. 4, 1912, p. 614.

The loss of weight noted represents the total amount of water-soluble material, including, in addition to all water-soluble salts and soluble organic ingredients, small quantities of substances extracted from the wood pulp, cereal products, or other carbonaceous absorbents.

EXAMINATION OF WATER EXTRACT.

It has been noted in the table of possible components shown on page 13 that the water extract of a low-flame explosive may contain a great variety of constituents, and attention has been called on page 17 to the difficulties often involved in definitely determining the manner in which the various bases and acid radicles were actually combined in the original explosive.

When qualitative tests have been obtained for several water-soluble ingredients, the method of mechanical examination (p. 17) or that of specific-gravity separation (p. 18) may give information as to exactly what combination of salts is present, so that the results of the separate determinations of bases and acid radicles may be properly interpreted.

The analysis of the water solution may involve many determinations which can be carried out by well-known methods described in reliable textbooks on quantitative analysis, such as the determination of chloride by precipitation as AgCl , of sulphate by precipitation as BaSO_4 , of oxalate by precipitation as CaC_2O_4 , and ignition to CaO , of carbonate by titration or evolution methods, or of potassium, magnesium, calcium, barium, zinc, and aluminum, by well-known gravimetric methods. These usual methods are employed in the bureau's laboratory, but are not discussed in this bulletin except where it is desired to emphasize some important feature.

It is customary to determine each constituent on a separate aliquot part of the water extract; usually 50 c. c. is taken for each determination. Duplicate analyses are made on parts of the two solutions representing the water extracts of the duplicate samples of the explosives.

DETERMINATION OF NONVOLATILE SOLIDS.

Aliquot 50 c. c. portions of the water extracts are evaporated to dryness in weighed platinum dishes on a steam bath, after about 1 or 2 c. c. of nitric acid has been added. If the solution contains sulphates, sulphuric acid is added instead of nitric. Also, if more than a small amount of chlorides is present, the evaporation with nitric acid should be carried out not in platinum dishes but in porcelain or silica dishes, because of the fact that chlorine liberated by the action of the nitric acid on chlorides will attack the platinum.

Dishes of pure fused silica ("Vitreosil" or other commercial product), about $3\frac{1}{2}$ inches in diameter, weighing 25 to 30 grams, are largely used in the bureau's laboratory and give satisfactory results.

IGNITION OF RESIDUE.

The residue from the evaporation is heated gently over a burner to volatilize ammonium salts and free acid, and burn off soluble organic matter. If the explosive contains organic materials such as wood pulp or cereal products, an appreciable quantity of soluble organic material will be found in the water solution. Experiments in the bureau's laboratory have shown that extraction with cold water may remove as much as 2 to 3 per cent from corn meal, 10 to 15 per cent from wheat flour (middlings), and 2 to 3 per cent from wood pulp. The water extract, therefore, may contain an amount, which depends on the proportion of carbonaceous material in the explosive, of dissolved organic material varying from a few tenths of 1 per cent to as much as 2 or 3 per cent, and also such soluble organic materials as are actual ingredients of the explosive.

After gentle ignition the residue is again treated with a small quantity of dilute acid, evaporated to dryness, and gently ignited until fuming ceases, or heated in an oven at about 120°C .

TREATMENT OF RESIDUE CONTAINING ZINC.

If the original sample of explosive contained ammonium nitrate and zinc oxide, the zinc oxide will have been mostly dissolved in the water solution by the action of the ammonium nitrate, and, in case nitric acid has been added to the water solution, the zinc will be present as zinc nitrate in the residue left on evaporation. The zinc nitrate is readily converted by ignition to zinc oxide, and on heating the residue strongly an evolution of oxides of nitrogen accompanied by an appreciable bubbling of the fused residue is noted. This bubbling may occasion loss of the fused solids unless the heating is done with great care. It is therefore advisable not to attempt to convert the zinc nitrate to zinc oxide by ignition, but to leave it as zinc nitrate, by heating the residue just to its fusion point only, or heating it in an oven at about 120°C . for one hour. Either method will completely remove the free acid and leave the residue in the form of nitrates.

If sulphuric acid, instead of nitric acid, has been added to the water solution during evaporation, the evaporated residue will, on heating until fumes are no longer given off, remain as sulphates.

This treatment with acid, evaporation, and ignition or drying is repeated until the weight of residue is practically constant. The residue represents the total quantity of nonvolatile inorganic salts

in the water solution, in the form of nitrates or sulphates, depending on the method followed.

The value of this determination is obvious. For example, if the solution contained sodium nitrate, ammonium nitrate, zinc oxide, and sodium sulphate, the nonvolatile residue would contain Na_2SO_4 and ZnSO_4 . The use of the specific-gravity separation in the preliminary qualitative examination (p. 18) would easily have indicated the presence of sodium sulphate and sodium nitrate. The Na_2SO_4 is determined gravimetrically as BaSO_4 in an aliquot part of the water extract. The nonvolatile residue obtained by evaporation of the water extract is redissolved, the zinc determined by precipitation as ZnCO_3 and ignition to ZnO , and this weight of ZnO calculated to an equivalent weight of ZnSO_4 . The weight of Na_2SO_4 found plus the weight of ZnSO_4 is then deducted from the total weight of residue found by evaporation as sulphates, the difference being equal to the NaNO_3 content in terms of Na_2SO_4 . The equivalent amount of NaNO_3 is then readily calculated. The NH_4NO_3 in the water extract is then determined by using another aliquot portion of the solution, and should be approximately equal to the total weight of water-soluble material minus the sum of the Na_2SO_4 , NaNO_3 , and ZnO contents, unless the extract contains an appreciable amount of soluble organic material.

DETERMINATION OF AMMONIUM SALTS AS NH_3 .

Ammonium salts are determined by the well-known method of distillation. An excess of strong KOH solution is added to an aliquot part of the water extract in a Kjeldahl or other distillation flask, the NH_3 is distilled into a known volume of standard H_2SO_4 solution, and the excess of acid titrated with standard alkaline solution, cochineal being used as the indicator. This method has been previously described in Bulletin 51.*

DETERMINATION OF ZINC.

As has been previously stated, when an explosive contains both zinc oxide and ammonium nitrate the zinc will be found mostly in the water extract, due to the solubility of the zinc oxide in ammonium nitrate.

The residue obtained by evaporation of the water extract is redissolved in dilute HCl, and the zinc precipitated as ZnCO_3 by carefully adding Na_2CO_3 until a slight turbidity shows on stirring. The mixture is then heated to boiling and filtered while hot through a Gooch crucible. If the solution is not alkaline after boiling, as may be

* Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, pp. 58-59.

readily determined by adding a few drops of phenolphthalein solution, more Na_2CO_3 is added until the red color of the indicator persists. The ZnCO_3 in the Gooch crucible is then ignited to ZnO and weighed.

Other alternative methods for determining zinc have been described in Bulletin 51,^a but the above method has been found entirely satisfactory.

DETERMINATION OF POTASSIUM.

PERCHLORATE METHOD.

Potassium is determined by the well-known method of precipitation with platinic chloride or by the perchlorate method of Sérullas.^b The perchlorate method depends upon the fact that potassium perchlorate is practically insoluble in alcohol, whereas the perchlorates of the other bases which might be present are more or less readily dissolved by this solvent.

The water solution containing potassium salts must be free from sulphuric acid or sulphates; if it does contain them they can be removed by precipitation with BaCl_2 and filtration. The solution is then evaporated to dryness and all acid fumes and ammonium salts driven off. The residue is dissolved in 50 c. c. of hot water containing considerably more than enough perchloric acid to combine with all the bases. Usually 5 to 6 c. c. of perchloric acid solution of 1.12 specific gravity is sufficient. This solution is obtainable from chemical dealers or may be prepared in the laboratory.^c Evaporate the mixture until it is thick, add a little more hot water and 5 to 6 c. c. more of the perchloric acid, and continue the evaporation, with stirring. Then heat the residue on a sand bath until dense white fumes are evolved. The cooled residue is then stirred with 20 c. c. of 97 per cent alcohol containing 0.2 per cent by weight of perchloric acid, and transferred to a Gooch crucible, using 20 c. c. more of the same alcohol solution. The residue of potassium perchlorate in the Gooch crucible is then washed with about 20 c. c. of a mixture of equal volumes of ether and alcohol, dried at 120 to 130° C., and weighed.

The barium perchlorate is readily soluble in the alcohol used, and magnesium does not interfere if the excess of perchloric acid is large enough. Ammonium salts should be removed, as has been stated, because ammonium perchlorate is not readily soluble in alcohol.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, p. 58.

^b Sérullas, —, Crystallization de l'acide oxichlorique (perchlorique), et sur quelques propriétés nouvelles de cet acide: Ann. chim. phys., t. 46, 1831, p. 294; see also Wiley, H. W., Principles and practice of agricultural analysis, vol. 2, 1908, pp. 578-593.

^c See Willard, H. H., Preparation of perchloric acid: Jour. Am. Chem. Soc., vol. 34, 1912, pp. 1480-1485; and Kreider, D. A., The preparation of perchloric acid and its application to the determination of potassium: Am. Jour. Sci., ser. 3, vol. 49, 1895, p. 443.

The method has been employed in the bureau's laboratory with good results and is more convenient than the platinic chloride method.

The following results are given as an example of the accuracy of the method and to show that the presence of sodium nitrate does not interfere with the determination of the potassium salt.

Results of determination of potassium nitrate in presence of sodium nitrate by perchlorate method.

Weight of KNO_3 and NaNO_3 used.		Weight of KClO_4 obtained.	Weight of KNO_3 found.	Error of determination.
KNO_3 .	NaNO_3 .			
Gram. 0.2500 .2500	Gram. 0.2500 .2500	Gram. 0.3414 .3420	Gram. 0.2491 .2495	Gram. -0.0009 -.0005

DETERMINATION OF NITRATES BY NITROMETER METHOD.

Nitrates in the water solution may be determined by means of the nitrometer as described in Bulletin 51.^a An aliquot part of the water solution, containing not more than the nitrogen equivalent of 0.8 gram of NaNO_3 or 1 gram of KNO_3 , is evaporated nearly to dryness on the steam bath and completely transferred, by means of as little water as possible, to the nitrometer generating bulb. Then 30 to 40 c. c. of 95 to 96 per cent H_2SO_4 is added slowly in small quantities to avoid overheating, and the generator shaken 8 to 10 minutes, when the volume of gas (NO) is measured and the percentage of nitrate calculated. It is necessary to use a larger volume of H_2SO_4 and to shake longer than is required in the determination of nitroglycerin because of the dilution of the acid by the water used for transferring the sample from the dish to the generator. The method gives accurate results if care is taken to insure that the reaction in the nitrometer is complete, by shaking for a sufficient length of time.

DETERMINATION OF NITRATES BY NITRON METHOD.

The determination of nitrates by the "nitron" method of Busch^b has been described in a number of textbooks^c but has not found general use in technical laboratories. It gives very reliable results when carried out with proper care and is here described in detail.

"Nitron," or 1:4 diphenyl 3:5 endoanilodihydrotriazol ($\text{C}_{20}\text{H}_{16}\text{N}_4$), forms an addition product with one molecule of HNO_3 , which is only slightly soluble in cold water.

^a Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite: Bull. 51, Bureau of Mines, 1913, p. 45.

^b Busch, M., Gravimetrische Bestimmung der Salpetersäure: Ber. deut. chem. Gesell., Jahrg. 38, 1905, p. 861; Gutbier, A., Die gewichtsanalytische Bestimmung der Salpetersäure mittels "Nitron" nach M. Busch: Ztschr. angew. Chem., Jahrg. 18, 1905, p. 494; Hes A., Über die gewichtsanalytische Bestimmung der Salpetersäure: Ztschr. anal. Chem., Jahrg. 48, 1909, p. 81.

^c Escales, R., Die Schiessbaumwolle, 1905, p. 218; Lunge, G., and Berl, E., Chemisch-technische Untersuchungsmethoden, Bd. 1, 1910, p. 391.

PREPARATION OF REAGENT.

To prepare the reagent, 1 part of nitron is dissolved in 9 parts of 5 per cent acetic acid with the aid of heat, filtered, and placed in a dark bottle. The solution decomposes in the light and does not keep well, hence it is best to prepare it in small quantities as needed.

METHOD OF PROCEDURE.

To the solution of nitrate, containing preferably not over 0.10 to 0.15 gram of nitrate, diluted to about 80 c. c., add 12 to 15 drops of dilute H_2SO_4 , heat to the boiling point, add 12 to 15 c. c. of the nitron reagent, stir and let stand one-half to three-fourths hour. Long, silky, needlelike crystals of the nitron nitrate separate out on cooling. Place the beaker in ice water for one to two hours and then filter off the crystals in a Gooch crucible, using slight suction. Wash with 10 c. c. of water cooled to 0°C ., and added in quantities of 1 to 2 c. c. at a time, using a part of the filtrate for washing out the beaker. Dry the precipitate at 105° to 110°C . until constant weight is obtained; about one hour is usually sufficient. To insure complete precipitation the filtrate is heated to boiling, a little more of the reagent added, and the mixture cooled as before.

The molecular weight of nitron is 312, of nitron nitrate 375. Thus, the nitrate being six times as heavy as HNO_3 , an error in the weight of the precipitate is reduced to one-sixth when expressed as HNO_3 , or to one-twenty-seventh when expressed as N.

The equation for converting the weight of nitron nitrate to the equivalent weight of sodium nitrate is as follows:

$$\frac{\text{Weight of nitron nitrate} \times 85}{375} = \text{Weight of sodium nitrate.}$$

INTERFERENCE OF OTHER SALTS.

Busch^a states that moderate amounts of chlorides or sulphates do not interfere with the determination of nitrate, but that bromides (solubility 1:800), iodides (1:20,000), chromates (1:6,000), chlorates (1:4,000), and perchlorates (1:50,000) are precipitated by the nitron reagent.

SOLUBILITY OF NITRON NITRATE.

Collins^b found that 0.45 per cent of the nitron-nitrate precipitate dissolved in 10 c. c. of ice water. The writer has found that if the weighed precipitate from 0.15 gram of KNO_3 is treated in the Gooch crucible with 10 c. c. of ice water in the same manner as in washing,

^a Busch, M., loc. cit.

^b Collins, S. W., The "nitron" method for the estimation of nitric acid: Analyst, vol. 32, 1907, p. 349.

an average loss of 0.61 per cent results. This agreed closely with the average result of 99.4 per cent obtained in determinations of pure KNO_3 .

RECOVERY OF NITRON.

The excess nitron in the filtrates and washings and the nitron contained in the precipitated nitron nitrate may be recovered as follows:

The filtrates and washings are made slightly alkaline with NH_4OH and the precipitated nitron filtered and washed with water. The nitron-nitrate precipitate is added to dilute NH_4OH , warmed to 60°C ., the precipitated nitron quickly filtered under slight pressure, washed with cold water, and dried in a vacuum. Decomposition may be avoided by conducting the filtering and washing in an atmosphere of inert gas and as much as possible away from the light.

DETERMINATION OF CHLORATES.

Two methods for the determination of chlorates are employed in the bureau's explosives laboratory, both giving excellent results and offering numerous advantages over many of the more laborious methods described in the literature and in the textbooks.

DETERMINATION OF CHLORATE BY REDUCTION WITH SULPHUR DIOXIDE.

Sulphur dioxide readily reduces chlorate to chloride in water solution. Its use in quantitatively determining chlorate is briefly mentioned by Gody,^a but no reference to it has been found by the writer in any textbook on analytical methods.

The method is as follows: An aliquot part of the water extract of an explosive, preferably containing not more than about 0.50 gram of chlorate, is treated with a current of gaseous sulphur dioxide—which may be conveniently obtained from small cylinders of liquid sulphur dioxide, from which the current of gas can easily be regulated by means of a valve—until a strong odor of the gas persists in the solution after stopping the current and blowing across the surface of the liquid. The reduction of the chlorate is accompanied by a slight rise in temperature of the liquid, a strong solution of chlorate becoming quite warm if the sulphur-dioxide current is rapid. After complete saturation with sulphur dioxide the liquid is boiled to remove any excess of it. It is advisable, even when its odor is no longer noted, to insure its complete removal by adding a few cubic centimeters of hydrogen-peroxide solution, which oxidizes the last traces of SO_2 to H_2SO_4 . The solution is then treated with a few drops of nitric acid and the chloride resulting from reduction of the chlorate is determined in the usual manner by precipitation with

^a Gody, L., *Traité theorique et pratique des matières explosives*, 1907, p. 245.

silver nitrate, and weighing as AgCl. The accuracy of the method is shown by the following results on weighed quantities of pure potassium chlorate.

Results of determinations of pure potassium chlorate by SO_2 -reduction method.

Test No.	Weight of KClO_3 used.	Weight of AgCl found.	KClO_3 found.	
			Weight.	Proportion of original quantity.
	Gram.	Gram.	Gram.	Per cent.
1.....	0.2500	0.2917	0.2494	99.76
2.....	.2500	.2918	.2495	99.80
3.....	.2500	.2915	.2492	99.68
4.....	.2500	.2919	.2496	99.84
Average.....				99.71

It must be noted that the complete removal of the sulphur dioxide from the solution is necessary in order to avoid reduction of the silver nitrate.

DETERMINATION OF CHLORATE BY REDUCTION WITH FORMALDEHYDE.

Formaldehyde in the form of the commercial solution called "formalin," containing approximately 40 per cent of gaseous formaldehyde, is also an effective and convenient reducing agent for quantitatively converting chlorate to chloride. Grützner^a called attention to the reduction of potassium chlorate by means of formaldehyde, and noted that the method might be employed for the quantitative determination of chlorates. The same reaction was discovered independently by the writer in 1911 and developed into an exact quantitative method for determining chlorates before the reference to Grützner's method had been noted. The results of the investigation of this method will be published as a separate paper, but the following brief description of the method will serve to indicate its application in the determination of chlorates in explosive mixtures.

A part of the water extract of the explosive, containing about 0.5 gram of chlorate, is diluted to about 150 c. c. and treated with 5 to 10 c. c. of a 40 per cent solution of formaldehyde, 2 c. c. of dilute nitric acid (1:3), and 50 c. c. of approximately $\frac{N}{10}$ silver nitrate solution. The beaker containing the mixture is covered with a watch glass and heated on the steam bath for $3\frac{1}{2}$ to 4 hours, after which the precipitated silver chloride may be at once filtered off, washed, dried, and weighed. The period of heating on the steam bath may be

^a Grützner, B., Ueber Formaldehyd als Reduktionsmittel und über eine neue quantitative massanalytische Bestimmung desselben. (A volumetric or gravimetric method for the determination of formaldehyde): Arch. Pharm., Bd. 234, 1896, p. 634; Ztschr. anal. Chem., Jahrg. 36, 1897, p. 527.

shortened to 2 hours if the mixture is afterwards allowed to stand overnight before filtering. Boiling the solution causes loss of some chlorine compound and makes the results low.

The following tabulation of a few results taken at random from a large number of tests made as described above shows that the method gives remarkably accurate results.

Results of determinations of pure potassium chlorate by the formaldehyde reduction method.

Test No.	Weight of KClO ₃ used.	Weight of AgCl found.	KClO ₃ found.	
			Weight.	Proportion of original quantity.
	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Per cent.</i>
1.....	0.5002	0.5855	0.5006	100.08
2.....	.5003	.5850	.5002	99.98
3.....	.5002	.5841	.4994	99.84
4.....	.5004	.5850	.5002	99.95
5.....	.5002	.5848	.5000	99.96
6.....	.5000	.5840	.4993	99.86
7.....	.5003	.5850	.5002	99.98
Average.....				99.95

DETERMINATION OF PERCHLORATES.

Several methods for the determination of perchlorates have been investigated in the explosives laboratory of the bureau, and the fusion method and the nitron method have been selected as the most convenient and satisfactory.

FUSION METHOD.

The fusion method consists in converting the perchlorate to chloride by fusion with anhydrous sodium carbonate and determining the resulting chloride by the usual method of precipitation as silver chloride.*

To determine the perchlorate in a water solution, an aliquot part of the solution is evaporated to a small volume and completely transferred to a 25-c. c. platinum crucible, where evaporation is continued until the volume is about 5 c. c. Anhydrous sodium carbonate is then added to the solution in the crucible until the crucible is completely full of the powder. The small amount of solution is absorbed by the sodium carbonate, and is readily dried out by careful heating with a small flame or on a steam bath or hot plate, after which the mass is heated over a burner until no evolution of gas bubbles is noted. The time of fusion is usually 15 to 20 minutes. The melt is then cooled, dissolved in dilute nitric acid, and the chloride determined by precipitation with silver nitrate.

* Förster, O., Mittheilungen aus der analytischen Praxis; Bestimmung von Perchlorat in Chlissalpetre: Chem. Ztg., Jahrg. 22, 1898, p. 357.

If both chloride and chlorate are present in addition to perchlorate, this determination gives the sum of all three of these ingredients weighed as silver chloride. A separate determination of chlorate by one of the methods described on pages 62 and 63 gives the chlorate and chloride together as chlorides, and a further separate determination is made of the chloride content in the original solution. From these results the amount of perchlorate actually present is readily calculated.

NITRON METHOD FOR DETERMINATION OF PERCHLORATES.

It has been noted (p. 61) that perchlorates are precipitated by nitron, and therefore interfere with the determination of nitrates by the nitron method when both nitrates and perchlorates are contained in the same solution. The extraordinarily low solubility of nitron perchlorate (according to Busch,* 1:50,000) suggested the use of the nitron method for determining perchlorates, and a limited number of trials has justified the conclusion that perchlorates, in the absence of interfering salts, such as nitrates, chlorates, bromides, iodides, chromates, and picrates, may be accurately determined by precipitation as nitron perchlorate.

The determinations were carried out by exactly the same method as has been described in pages 60 to 62 for determining nitrates, about 0.12 gram of supposedly pure ammonium perchlorate being used for each test. The weight of nitron perchlorate ($C_{20}H_{16}N_4 \cdot HClO_4$) found, multiplied by the molecular weight of ammonium perchlorate (117.5) and divided by the molecular weight of nitron perchlorate (412.5), is equal to the weight of ammonium perchlorate. Two determinations showed the ammonium perchlorate to have a purity of 99.67 and 99.58 per cent, respectively, whereas several determinations by the fusion method (p. 64) gave a purity of 99.53 per cent.

DETERMINATION OF NITRATES, CHLORIDES, CHLORATES, AND PERCHLORATES IN A MIXTURE.

A water extract containing nitrates, chlorides, chlorates, and perchlorates may be analyzed by proper application of the methods described in the preceding pages of this bulletin.

Chlorides are determined gravimetrically or volumetrically by precipitation with $AgNO_3$. Chlorates are determined by reduction with SO_2 gas (see p. 62) or formaldehyde (see p. 63) and precipitation of the resulting chloride with $AgNO_3$, the result being corrected for the chloride originally present as such.

* Busch, M., Gravimetrische Bestimmung der Salpetersäure: Ber. deut. Chem. Gesell., Jahrg. 38, 1905, p. 861.

Perchlorates are determined by fusing with Na_2CO_3 and precipitation with AgNO_3 (see p. 64), the total chloride thus formed being corrected for the quantity originally present plus the quantity equivalent to the chlorate originally present. Nitrates are determined by reducing the chlorate to chloride with SO_2 gas, boiling off the free SO_2 , precipitating the combined nitrate and perchlorate with nitron (see pp. 60 and 65), and correcting the total weight of nitron nitrate and nitron perchlorate for the weight of nitron perchlorate equivalent to the perchlorate found by the fusion method.

Obviously, each of these determinations must be made on a separate part of the water solution.

DETERMINATION OF SOLUBLE ORGANIC MATERIALS IN THE WATER EXTRACT.

In addition to those organic substances extracted from the carbonaceous combustible material which have been mentioned, such soluble organic substances as sugars and gums may be contained in the water extract as actual constituents of the explosive mixture.

DETERMINATION OF SUGARS.

The total sugars present are determined as follows: An aliquot part of the water extract is acidified with HCl (1 c. c. of strong HCl to 100 c. c. of solution), heated gradually just to the boiling point in order to invert cane sugar, and then cooled. The acidity is nearly neutralized with Na_2CO_3 , an excess of Fehling's solution added, and the mixture heated on the steam bath until reduction is complete. An excess of Fehling's solution is indicated by the blue color of the supernatant liquid after the precipitate has settled. The precipitated Cu_2O is filtered off in a Gooch crucible, dried, ignited to constant weight, and weighed as CuO , or merely dried and weighed as Cu_2O .

A blank determination is made by heating an equal volume of Fehling's solution as in the determination of the sugar, filtering off any separated Cu_2O , igniting to CuO , and weighing. This weight of CuO is deducted from that obtained in the determination of the sugar. The weight of CuO multiplied by the factor 0.4308 equals the weight of cane sugar, and the corresponding factor for Cu_2O is 0.4790.*

In order to determine the amount of sugar in the water extract which might result from cereal products in the explosive, samples of corn meal, wheat flour (middlings), and wood pulp were extracted, first with ether to remove oils, then with cold water, and the total sugars in the water extracts determined. The amounts of sugars found were: In corn meal 2.65 per cent, in wheat middlings 6.25 to 7 per cent, in wood pulp 0.17 to 0.62 per cent. Thus if an explosive contained 25

* Allen, A. H., Commercial organic analysis, vol. 1, 1905, p. 284.

per cent of wheat middlings, its water extract might show a sugar content of as much as 1.75 per cent, derived from extraction of the middlings and not present as an actual constituent of the explosive.

DETERMINATION OF GUM ARABIC.

Gum arabic is used in certain granular explosives as a binding material for the purpose of agglomerating the various constituents of the explosive into more or less regular granules. The gum arabic, being entirely soluble in water, is found in the water extract and may be determined with approximate accuracy by precipitation with basic lead acetate. The precipitate formed is white, flocculent, and bulky.

Because of the fact that its composition is not definite, it is necessary to make use of a factor obtained from the results of precipitating a known weight of gum arabic from its water solution by the method employed in making the determination on an unknown solution.

The following method of procedure has been found to give satisfactory results:

A solution of basic lead acetate is prepared by adding 150 grams of normal lead acetate and 50 grams of lead oxide (PbO) to 500 c. c. of distilled water, heating the mixture almost to boiling, and filtering. Then 0.10 gram of powdered gum arabic is dissolved in cold water and basic lead acetate solution is added with stirring until no further precipitation results; the mixture is then allowed to stand for several hours, the precipitate filtered into a weighed Gooch crucible, washed several times with absolute alcohol, dried at 100°C. , and weighed. Several determinations gave an average of 0.2012 gram of the precipitate from 0.10 gram of gum arabic. The factor for calculating the weight of gum arabic from the weight of the precipitate is therefore $\frac{0.1000}{0.2012} = 0.4971$.

The determination of the gum arabic in a solution is carried out in exactly the above manner. The weight of precipitate multiplied by the factor 0.4971 gives the weight of the gum arabic content.

Most of the usual water-soluble constituents of explosives do not interfere with the determination of gum arabic. Any chlorides must, however, be removed by precipitation with silver nitrate, as the precipitation of lead chloride in the cold solution would cause high results.

EXTRACTION WITH DILUTE HYDROCHLORIC ACID.

The principal substances soluble in cold dilute hydrochloric acid are the antacids added to the explosive to neutralize any acidity that may be present or might later develop in some constituent of the

explosive. The antacids generally used are calcium or magnesium carbonates or zinc oxide; the zinc oxide is usually found in the water solution if the explosive contains NH_4NO_3 . Other substances, more or less soluble in dilute hydrochloric acid, that may form part of the explosive are metallic zinc, aluminum, manganese dioxide, and ferric oxide. A sample of a commercial explosive, recently examined in the bureau's laboratory, contained calcium silicide.

Extraction with cold dilute hydrochloric acid is resorted to only when the explosive contains no starch. When the explosive contains cereal products this cold acid treatment is dispensed with and the acid-soluble inorganic substances are removed with the starch in one operation by hydrolysis with boiling dilute acid.

EXTRACTION WITH COLD DILUTE ACID.

The extraction with cold acid is carried out in the same manner as the water extraction, using the suction flask fitted with rubber stopper and carbon tube, Spencer funnel, or other device for holding the filtering crucible. The crucibles containing the dried and weighed residues left after extraction with water are placed in the carbon tubes or other holders, and dilute hydrochloric acid (1:10) added. After standing for a short time this acid is drawn through into the flask by means of suction, and a fresh portion of the acid added. This treatment is continued until 100 c. c. of the 1:10 acid has passed through the sample in each crucible. The excess of acid is then removed from the samples with several washings of water, and the crucibles containing the insoluble residue dried as before for at least 5 hours at 95° to 100° C. and weighed at once after cooling in a desiccator.

HYDROLYSIS WITH BOILING DILUTE HYDROCHLORIC ACID.

If the explosive contains starch the extraction with cold acid is usually omitted and the hydrolysis of the starch carried out as follows:

The water-insoluble residues in the crucibles are moistened with a little water and completely transferred by means of a spatula, or with a stream of water from a wash bottle, to 500 c. c. beakers. If Gooch crucibles are used, the asbestos mats are removed together with the residues and the crucibles are dried and weighed. The weight of asbestos thus determined by difference from the original weights of the prepared crucibles is deducted from the final weight of dry residue remaining after hydrolysis. Water is added to the beakers until the total volume is about 300 c. c., then about 3 c. c. of strong hydrochloric acid (specific gravity 1.2) is added and the mixture

boiled until the starch is completely hydrolyzed, a drop of the solution being tested from time to time on a spot plate with a solution of iodine in potassium iodide until a blue coloration no longer appears.

The insoluble residue is then filtered onto a fresh Gooch crucible or through the original porous crucible, if such was used, washed with water to remove all free acid and dissolved material, dried as before, and weighed, the weight being corrected for the weight of the asbestos mat from the original crucible.

In addition to hydrolyzing the starch to soluble dextrine and dissolving the antacid present, the boiling with dilute acid removes certain soluble parts of the wood pulp, and it is therefore necessary that the boiling should be continued only long enough completely to hydrolyze the starch, and also that the strength of the acid should be no greater than that indicated (approximately 1:100). The effect of the use of stronger acid is shown in the following experiments on three samples of wood pulp:

SOLUBILITY OF WOOD PULP IN BOILING HYDROCHLORIC ACID OF VARYING DILUTION.

The samples of wood pulp were extracted with ether, dried, then extracted with cold water, and again dried. Two-gram parts of the extracted, dried samples of wood pulp were then boiled for 15 minutes each with 250 c. c. of water to which strong hydrochloric acid in quantities varying from 2.5 to 25 c. c. had been added. The residues were then filtered, washed, dried, and weighed. For comparison another 2-gram part of each dried sample was extracted with 250 c. c. of cold, dilute acid (1:10), washed, dried, and weighed.

Loss of wood pulp in weight on boiling with hydrochloric acid of different concentrations.

Volume of water used.	Volume of acid added.	Loss in weight.		
		Sample 157.	Sample 158.	Sample 175.
<i>C. c.</i>	<i>C. c.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
250	2.5	11.71	10.35	12.55
250	5.0	14.44	13.25	15.35
250	10.0	18.10	17.95	19.85
250	20.0	21.17	23.95	22.92
250	25.0	22.63	23.21	25.91

By extraction with 250 c. c. of cold acid (1:10) sample 157 lost 3.60 per cent, sample 158 lost 3.97 per cent, and sample 175 lost 4.10 per cent, respectively.

It was observed that as the concentration of the acid was increased the solubility of the wood-pulp samples increased. Even with 1 part

acid to 100 parts water, over 10 per cent of the original dry weight of wood pulp was dissolved by boiling.

EXAMINATION OF ACID SOLUTION.

The inorganic substances dissolved by either the extraction with cold hydrochloric acid (1:10) or boiling with dilute hydrochloric acid (1:100) are determined in the filtrates from the insoluble residue by the usual methods.

DETERMINATION OF ALUMINUM AND IRON.

Both aluminum and iron may be present in small proportions as impurities or in larger proportions if metallic aluminum powder or ferric oxide were used as actual ingredients of the original explosive.

If there are no metals other than Al, Fe, Ca, and Mg in the acid solution, the entire solution may be used for the successive determination of these substances but it is generally advisable to use only one-half, reserving the other half.

The acid solution is made slightly alkaline with NH_4OH and boiled for several minutes. If the precipitate of iron or aluminum hydroxides is very small, it may be disregarded and the calcium precipitated without previous filtration, otherwise the solution is filtered and the precipitate dried at 100°C ., ignited, and weighed as Fe_2O_3 or Al_2O_3 . If qualitative tests have been obtained for both iron and aluminum, the ignited oxides may be fused with potassium bisulphate, the fused mass dissolved in dilute H_2SO_4 , the dissolved iron reduced to the ferrous condition by passing H_2S through the boiling solution, the free H_2S displaced from the solution by a current of CO_2 , and the iron determined by titration with standard potassium permanganate solution.*

DETERMINATION OF CALCIUM.

The filtrate from the determination of iron and aluminum is used for the determination of calcium. More NH_4OH is added if the solution is not already strongly ammoniacal, the liquid heated to boiling, hot ammonium oxalate solution added in slight excess, and the boiling continued for several minutes. The precipitate is allowed to settle completely and then is filtered, washed, ignited, and weighed as CaO .

DETERMINATION OF MAGNESIUM.

Magnesium is determined in the filtrate from the calcium determination by evaporating to about 100 c. c., adding an excess of a solution of sodium hydrogen phosphate to the hot solution, then a

* Treadwell, F. P., Analytical chemistry, vol. 2, 1910, p. 103.

large excess of NH_4OH , and allowing the precipitate to settle for several hours. The precipitate is filtered, washed, ignited, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

DETERMINATION OF ZINC.

Any zinc which may be contained in the acid solution is determined in a separate aliquot part of the solution by precipitation with Na_2CO_3 , as described on page 58.

DETERMINATION OF MANGANESE DIOXIDE.

Manganese dioxide, if the explosive contains it, will be only partly dissolved by extraction with cold dilute HCl (1:10) or by boiling with dilute HCl (1:100) to hydrolyze the starch.

The manganese dissolved in the acid solution is determined by concentrating a part of the solution and oxidizing to Mn_2O_7 by means of HNO_3 and KClO_3 crystals. The precipitated Mn_2O_7 is filtered off, ignited, and weighed. That part of the MnO_2 in the insoluble residue from the extraction with acid is determined by igniting to drive off the organic material, leaving the manganese in the form of Mn_2O_7 , which is weighed direct.

A mixture of metallic zinc, manganese dioxide, and flour left after extraction with water was analyzed as follows: The mixture was transferred from the crucible to a beaker, treated with boiling dilute HCl (1:100) to hydrolyze the starch and dissolve the metallic zinc, a part of the MnO_2 also being dissolved. The residue was ignited and weighed as Mn_2O_7 . The filtrate was evaporated to dryness with H_2SO_4 and ignited to convert the dissolved zinc and manganese to sulphates. These ignited sulphates were dissolved in a little water, and, without filtering off the small quantity of Mn_2O_7 resulting from decomposition of the MnSO_4 , the solution was treated with an excess of strong HNO_3 and evaporated on the steam bath, with the frequent addition of crystals of potassium chlorate. The residue obtained by evaporation to complete dryness was redissolved in water, the Mn_2O_7 resulting from oxidation of the MnSO_4 was filtered, washed, ignited, and weighed. The zinc in the filtrate was determined by precipitation with Na_2CO_3 and ignition of the resulting ZnCO_3 to ZnO (see p. 58).

The total MnO_2 originally present was calculated from the combined weights of Mn_2O_7 obtained from the insoluble part and the acid solution.

DETERMINATION OF CALCIUM SILICIDE.

Although calcium silicide is a rather unusual ingredient of explosives, the fact that it is contained in at least one commercial

blasting explosive used in this country justifies a brief statement regarding its properties.

Calcium silicide (CaSi_2) is of value in explosive mixtures for the reason that its oxidation to CaO and SiO_2 produces a large amount of heat. It is a solid substance of lead-gray color, metallic luster, and scaly crystalline structure. On treatment with dilute hydrochloric acid it evolves a mixture of hydrogen and silicon hydride (SiH_4), the latter being spontaneously inflammable. This behavior serves as an excellent means of identifying calcium silicide.

The solution in hydrochloric acid may be used to determine the calcium, from which the amount of CaSi_2 may be calculated.

EXTRACTION WITH CARBON BISULPHIDE.

DETERMINATION OF SULPHUR.

Extraction with carbon bisulphide is necessary only when the explosive contains a large proportion of sulphur. The extraction with ether for the usual length of time will remove all of the sulphur if the amount is only a few per cent, but in case any considerable quantity of sulphur crystallizes out in the ether solution, it is advisable to extract with carbon bisulphide to insure complete removal of this constituent. The extraction is usually made on the dried and weighed residue remaining after extraction or boiling with dilute hydrochloric acid, and is carried out in the Wiley extraction apparatus in the same manner as the extraction with ether. After extraction with carbon bisulphide the excess solvent remaining in the crucibles is removed by suction, the crucibles left in a warm place until the odor of carbon bisulphide is no longer noted, and then placed in an oven at 95° to 100° C. to dry for 5 hours. Attention is called to the fact that the vapors of carbon bisulphide ignite at temperatures far below a red heat, hence there is danger in placing the crucibles wet with the solvent in the drying oven immediately after extraction.

The loss of weight of the residue is regarded as sulphur, or, in case freshly distilled carbon bisulphide has been used for the extraction, the extract may be evaporated in the bell-jar evaporator and the sulphur weighed direct. The weight of sulphur found by this extraction is added to that found in the ether extract.

EXTRACTION WITH ACETONE.

DETERMINATION OF NITROCELLULOSE AND NITROSTARCH.

Extraction with acetone is necessary only when the qualitative examination has indicated that the explosive contains nitrocellulose or nitrostarch.

Because of the fact that nitrocellulose is used in some explosives in very small amounts, its presence may readily be overlooked, especially if the explosive is not noticeably gelatinous in its consistency.

Both nitrocellulose and nitrostarch, being insoluble in ether, water, carbon bisulphide, and dilute hydrochloric acid, may be determined after all of these extractions have been made. It is important to note, however, that these organic nitrates are gradually decomposed by long-continued heating at temperatures as high as 100° C., and it is therefore advisable, when either nitrocellulose or nitrostarch have been found, that most of the drying, after the extractions with ether, water, etc., be done at a temperature of 70° C., with an additional half hour at 100° C. to insure constant weight.

METHOD OF TREATMENT WITH ACETONE.

The best method of dissolving nitrocellulose or nitrostarch by means of acetone is as follows: The residue is transferred from the crucible to a 100 c. c. beaker, the mat being left in the crucible if possible; the beaker is nearly filled with acetone, and the mixture permitted to stand for several hours with frequent stirring in order to insure complete solution. When gelatinous-like "flocks" no longer show in the solution, it is filtered through the original crucible, and the residue washed thoroughly with acetone. If the sample contains a large quantity of nitrostarch, as do some of the nitrostarch explosives, the solution may filter with difficulty; in that case the beaker should be allowed to stand until the insoluble residue has completely settled, the clear solution carefully decanted, and fresh acetone added to the insoluble residue before attempting to filter. In this manner most of the soluble material is removed before filtering, and the filter does not become so easily clogged.

The residue left in the filter after thorough washing with acetone is dried and weighed as usual, and the loss of weight regarded as nitrocellulose or nitrostarch, as the case may be. Which of these substances the explosive contains must be determined by microscopic examination as noted under "Qualitative Examination" (p. 15).

RECOVERY OF NITROCELLULOSE OR NITROSTARCH FROM ACETONE SOLUTION.

The organic nitrate dissolved in the acetone may be recovered by the following method: The acetone solution is slowly added, with continual stirring, to about twice its volume of water heated to 70° to 80° C., the mixture heated on the steam bath until all of the acetone has been evaporated, and the precipitated organic nitrate filtered off.

The precipitate may be dried and weighed, its weight serving as a check on the determination of loss of weight on extraction, and its nitrogen content determined by means of the nitrometer.

EXAMINATION OF THE INSOLUBLE RESIDUE.

The insoluble residue left after all extractions have been completed may contain any of the substances noted in the list of components on page 13. All of these substances have been found in permissible explosives tested by the bureau, and there are other ones possible which might be added to the list.

MICROSCOPIC EXAMINATION.

Absolute identification of the substances contained in the insoluble residue from the last extraction is frequently difficult and often is made possible only by means of a careful microscopic examination. Familiarity with the appearance of such materials under the microscope is therefore of great assistance.

Two types of microscopes have been found useful in the bureau's laboratory—a binocular microscope, by means of which magnifications from about 10 to 75 diameters may be obtained, and an ordinary petrographic microscope which gives magnifications ranging from about 20 to 300 diameters. The former type is the more valuable for the examination of coarse materials, because of the great depth of focus obtainable, whereas the petrographic microscope, with its higher powers of magnification, is useful for the identification of finer materials.

PREPARATION OF SLIDES.

Careful mounting of the samples for microscopic examination is not at all necessary. The usual method is to spread a small quantity of the dry residue uniformly over the surface of the glass microscope slide in a thin layer so that individual particles are separated from each other, placing the slide directly under the objective, without a cover glass.

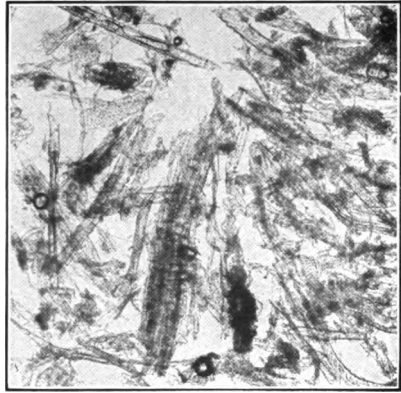
The most suitable magnification to use is determined by trial. A number of samples of different materials that may be found in the insoluble residue are shown in Plates I, II, and III under magnifications of 10 to 150 diameters.

In Plate I, *A* and *B*, is shown wood pulp of different grades; Plate I, *C*, shows fine sawdust with its characteristic bundles of fibers; in Plate I, *D* and *E*, different types of kieselguhr or infusorial earth are illustrated; and Plate I, *F*, shows the crude fiber from coarse wheat flour (middlings) left after hydrolysis of the starch.

A and *B*, Plate II, represent cotton (cellulose) and nitrocellulose, respectively, both of which appear alike under the microscope unless examined in polarized light, when the unnitrated fibers appear in brilliant colors and the nitrated fibers are dark; Plate II, *C*, repre-



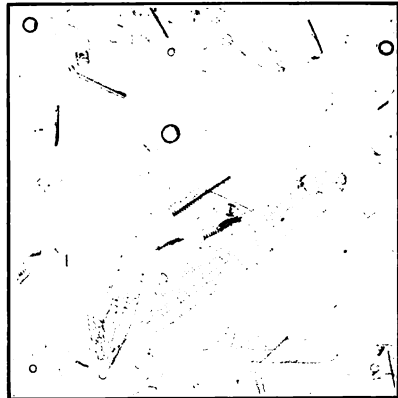
A. WOOD PULP NO. 1 ($\times 50$).



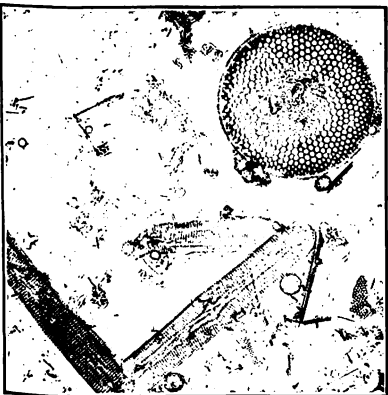
B. WOOD PULP NO. 2 ($\times 50$).



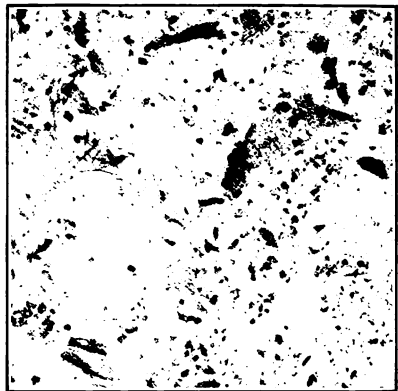
C. SAWDUST ($\times 25$).



D. INFUSORIAL EARTH NO. 1 ($\times 150$).



E. INFUSORIAL EARTH NO. 2 ($\times 150$).



F. CRUDE FIBER FROM WHEAT MID-
DLINGS ($\times 25$).

sents fine wheat flour; Plate II, *D*, fine wheat flour mixed with wood pulp; Plate II, *E*, coarse wheat flour (middlings); and Plate II, *F*, fine corn meal.

A number of the more unusual carbonaceous combustible materials used in explosives are illustrated in Plate III. In this plate *A* shows peanut-shell meal; *B*, rice hulls; *C*, corncob meal (commercially known as "Corona meal"); and *D*, "vegetable ivory" meal, a product obtained by pulverizing the waste resulting in the manufacture of buttons from "vegetable ivory" nuts ("corosos" nuts), the fruit of the *phytelephas macrocarpa* or "ivory nut" tree of tropical countries. The materials shown in Plate III have practically no absorbent properties, their chief use in explosives being to serve as combustible materials.

DETERMINATION OF ASH.

The determination of "ash" in an explosive, that is, natural inorganic insoluble constituents of the carbonaceous materials, plus any insoluble nonvolatile impurities in the various salts is, of course, possible only when no inorganic substances are actual constituents of the insoluble residue. The amount of such inorganic materials may be determined, however, by burning off the organic matter, as in the determination of ash, and weighing the resulting nonvolatile residue, which includes the ash.

One of the duplicate samples of the dried and weighed insoluble residue is used for the determination of ash, or of combined ash and inorganic substances. This residue may be ignited in the original filtering crucible in which it was dried, the organic material being burned by first heating it very gradually with a small free flame of a burner until combustible gases cease to be evolved, then increasing the size of the flame and tilting the crucible so that the carbon is finally burned off, leaving a constant weight of inorganic residue.

If desired, the ignition may be carried out in a platinum crucible by transferring to it all the dried and weighed residue from the original filtering crucible. This method involves an additional weighing (of the platinum crucible) but the combustion is more rapid in the platinum crucible than in the porcelain or alundum filtering crucibles.

The proportion of ash is usually not over 0.20 per cent. If it is over 0.5 per cent, the residue probably contains, in addition to the real ash of the carbonaceous materials, insoluble inorganic impurities from some of the saline ingredients, or possibly small amounts of added inorganic material, such as kieselguhr, clay, etc. A high ash content may also indicate that either the water or acid extractions

have not been complete. In this respect the determination of ash may be regarded as a check on the analysis.

THE ULTIMATE COMPOSITION OF CARBONACEOUS INGREDIENTS.

In making calculations of the reactions involved in the explosive decomposition of explosive mixtures for the purpose of calculating the temperatures, gas volumes, etc., resulting from explosion, it was essential that the average ultimate composition of the various carbonaceous ingredients be known so that the formulas used to represent the composition of these substances might be as nearly correct as possible.

ULTIMATE COMPOSITION OF WOOD PULP.

The results of analyses of different woods by various investigators were collected and averaged. A summary of these results is shown in the following table:

Results of analyses of woods by different investigators.

[Average ultimate composition.]

Designation of test.	Proportion of—			Authority.	Remarks.
	Carbon.	Hydrogen.	Oxygen. ^a		
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>		
A.....	49.77	6.15	44.08	Gottlieb ^b	Average of 7 kinds of wood.
B.....	49.50	6.00	44.50	Poole ^c	
C.....	50.64	6.17	43.19	Chevandier ^d	Average of 5 kinds of wood.
D.....	50.00	6.00	44.00	Aufhäuser ^e	
E.....	49.20	6.10	44.70	Chevandier ^f	Average of 13 kinds of wood.
F.....	50.00	6.00	44.00	Muck ^g	
Average....	49.85	6.07	44.08		

^a Includes small amount of nitrogen.

^b Poole, H., *Calorific value of fuels*, 1905, p. 86.

^c Poole, H., *op. cit.*, p. 85.

^d Gody, L., *Traité théorique et pratique des matières explosives*, 1907, p. 67.

^e Aufhäuser, —, *Die spezifischen Eigenschaften und Unterschiede der festen und flüssigen Brennstoffe und ihre technische Bedeutung*: Glückauf, Jahrg. 49, 1913, p. 604.

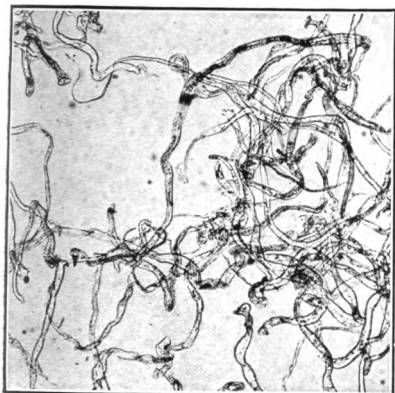
^f Jüptner, H. von, *Lehrbuch der chemischen Technologie der Energien*, Bd. 1, 1905, p. 154.

^g Jüptner, H. von, *op. cit.*, p. 170.

This average composition corresponds to the empirical formula $C_{15}H_{21.9}O_{9.9}$, or expressed in round numbers, $C_{15}H_{22}O_{10}$, which is the formula used by chemists of the bureau in previous works.^a

In order to check this result, by tests of wood pulp actually used in the manufacture of explosives in this country, samples of wood pulp were obtained from various manufacturers of permissible explo-

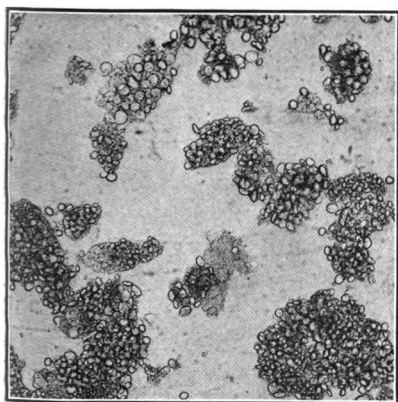
^a Hall, C., Snelling, W. O., and Howell, S. P., *Investigations of explosives used in coal mines*: Bull. 15, Bureau of Mines, 1912, p. 62.



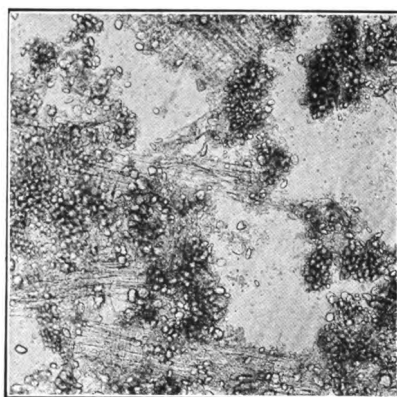
A. CELLULOSE (COTTON) ($\times 50$).



B. NITROCELLULOSE ($\times 50$).



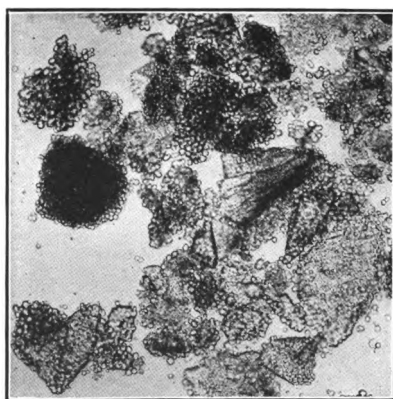
C. WHEAT FLOUR (FINE) ($\times 50$).



D. WHEAT FLOUR (FINE) AND WOOD PULP ($\times 50$).



E. WHEAT FLOUR (MIDDLINGS) ($\times 50$).



F. CORN MEAL ($\times 50$).

sives and submitted to careful ultimate analyses by the combustion method, with the following results:

Results of analyses of wood pulp used in explosives in the United States.

[Analyses made under direction of A. C. Fieldner.]

Designation of sample. (Lab. No.)	Composition of samples "as received."				Composition of samples calculated free from ash and moisture.		
	Moisture.	Ash.	Carbon.	Hydrogen.	Carbon.	Hydrogen.	Oxygen (by difference).
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
156.....	9.33	0.59	46.14	6.68	51.22	6.25	42.53
157.....	6.83	.70	47.20	6.37	51.04	6.07	42.89
158.....	6.53	.23	48.40	6.50	51.91	6.18	41.91
159.....	6.50	.24	47.53	6.42	50.99	6.11	42.90
163.....	7.35	.32	46.40	6.45	50.26	6.10	43.64
164.....	5.73	.38	48.19	6.35	51.32	6.09	42.59
165.....	9.30	.48	46.18	6.41	51.19	5.96	42.85
166.....	6.63	.46	47.40	6.44	51.03	6.13	42.84
167.....	6.90	.82	47.22	6.30	51.17	5.99	42.84
Average.....					51.12	6.10	42.78

The average composition of the nine samples of wood pulp—51.12 per cent carbon, 6.10 per cent hydrogen, and 42.78 per cent oxygen—does not differ widely from the average of the results found in the literature (see p. 76). The empirical formula calculated from these results is $C_{15}H_{21.5}O_{9.5}$, which, like the formula on page 76 may also be expressed as $C_{15}H_{22}O_{10}$.

This formula for wood pulp has therefore been accepted for use in calculations based upon the chemical reactions involved in the explosion of blasting explosives containing this ingredient.

ULTIMATE COMPOSITION OF CORN MEAL.

In view of the fact that no results of ultimate analyses of corn meal could be found in the literature on the subject, an attempt was made to calculate such an analysis from the results of average proximate analyses. The following was selected as an average proximate analysis of corn meal:^a

Composition of corn meal.

Constituent.	Proportion in corn meal.	
	By analysis.	Calculated on ash-free and moisture-free basis.
	<i>Per cent.</i>	<i>Per cent.</i>
Moisture.....	12.57
Proteids.....	7.13	8.13
Ether extract.....	1.33	1.52
Crude fiber.....	.87	.99
Carbohydrates.....	78.36	89.36
Ash.....	.61

^a Wiley, H. W., Composition of maize (Indian corn), including the grain, meal, stalks, pith, fodder, and cobs: Bureau of Chemistry, Department of Agriculture, Bull. 50, 1893, p. 13.

The composition of the proteid was assumed to be as follows: C, 55.22 per cent; H, 7.25 per cent; N, 16.15 per cent; S, 0.61 per cent; O, 20.77 per cent, this being the average composition of the zeins which compose the proteids.^a

The composition of the ether extract was calculated as C, 75.16 per cent, H, 11.72 per cent, and O, 12.69 per cent from the average of the compositions given by König^b and Hopkins.^c

The crude fiber was assumed to have the same formula as wood pulp, $C_{18}H_{22}O_{10}$, or approximately 49.72 per cent C, 6.08 per cent H, and 44.2 per cent O.

The carbohydrates were assumed to be sugar and starch, the sugar constituting 1.75 per cent of the total meal,^d or 2.22 per cent of the moisture-free and ash-free material.

If the above assumptions are accepted and the small proportion of sulphur in the proteids be disregarded, the ultimate composition of the moisture-free and ash-free material, calculated from the proximate analysis, is as follows: C, 45.77 per cent; H, 6.35 per cent; O, 46.51 per cent; N, 1.37 per cent. This composition gives approximately the empirical formula, $C_{15}H_{24}O_{11.4}N_{0.4}$.

The average of three analyses of corn meal, kindly reported to the writer by Prof. H. P. Ormsby, of Pennsylvania State College, is as follows: C, 46.46 per cent; H, 6.74 per cent; O, 45.06 per cent; N, 1.74 per cent. The formula calculated from this composition is $C_{15}H_{26}O_{10.9}N_{0.5}$, which agrees closely with the formula calculated from the proximate analysis.

Both of these results were closely confirmed by the results of two analyses of corn meal by A. C. Fieldner, of the Bureau of Mines, which averaged 46.87 per cent C, 6.50 per cent H, 45.43 per cent O, 1.20 per cent N, corresponding to the formula $C_{15}H_{25}O_{11}N_{0.3}$.

The average of the three formulas obtained as above noted is $C_{15}H_{25}O_{11.1}N_{0.4}$, which, for all practical purposes, may be written $C_{15}H_{25}O_{11}$. It is believed that this formula approximates the average composition of dry corn meal, and may be used in calculations where a formula for corn meal is required.

ULTIMATE COMPOSITION OF WHEAT FLOUR.

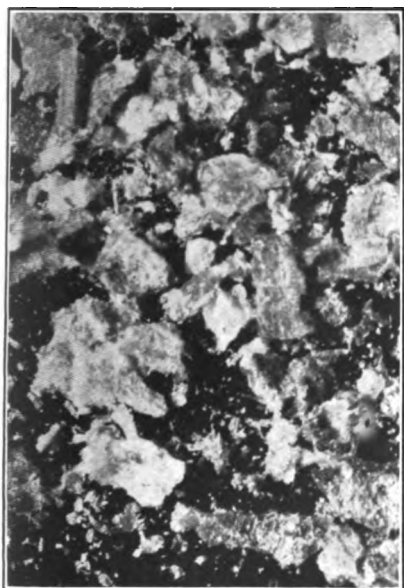
The ultimate composition of wheat flour, or middlings, was calculated, by the method used for corn meal, from an average of a large number of proximate analyses. The calculated composition

^a Wiley, H. W., Composition of maize (Indian corn), including the grain, meal, stalks, pith, fodder, and cobs: Bureau of Chemistry, Department of Agriculture, Bull. 50, 1898, p. 9.

^b Blyth, A. W., and Blyth, M. W., Foods, their composition and analysis, 1903, p. 216.

^c Benedikt-Ulzer, Analyse der Fette und Wachstern, Auf. 5, 1908, p. 715.

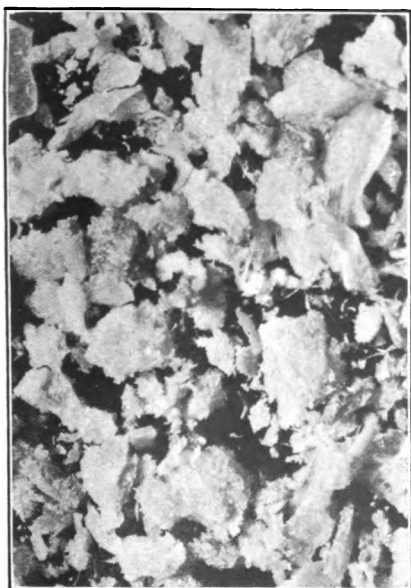
^d Bryan, A. G., Given, A., and Straughn, M. N., Extraction of grains and cattle foods for the determination of sugars; a comparison of the alcohol and the sodium digestions: Bureau of Chemistry, Department of Agriculture, Circular 71, 1911, 14 pp.



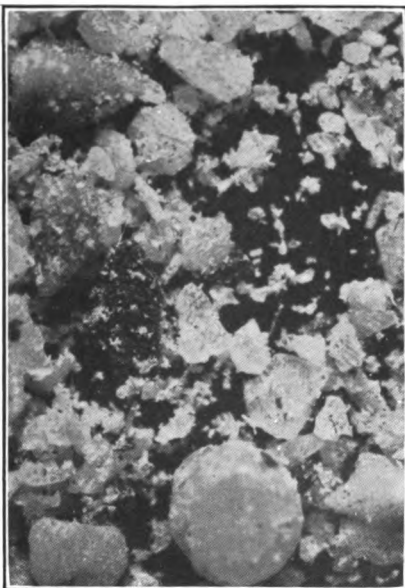
A. PEANUT-SHELL MEAL ($\times 15$).



B. RICE HULLS ($\times 15$).



C. CORNCOB MEAL ($\times 15$).



D. VEGETABLE-IVORY MEAL ($\times 15$).

was 46.65 per cent C, 6.43 per cent H, 44.10 per cent O, 2.67 per cent N, 0.15 per cent S, and corresponds to the formula $C_{15}H_{24.8}O_{10.6}N_{0.7}$ (the sulphur being disregarded).

Four samples of wheat middlings analyzed by A. C. Fieldner gave an average composition of 46.46 per cent C, 6.44 per cent H, 44.61 per cent O, 2.33 per cent N, and 0.16 per cent S, a composition that corresponds to the formula $C_{15}H_{25}O_{10.8}N_{0.6}$.

Both of these formulas may, like those for corn meal, be expressed as $C_{15}H_{25}O_{11}$, which formula, it is considered, may be used in explosives calculations as being approximately accurate for dry wheat flour, or middlings.

CONCLUDING REMARKS.

In describing the methods employed by the Bureau of Mines for the analysis of explosives submitted for tests, it has been impossible to discuss in detail the methods used for the analysis of all the various combinations of ingredients which have been found in the many different explosives examined, or which may be met with in explosives submitted in the future. It has frequently been necessary to devise methods for the analysis of some unusual mixture of ingredients in an explosive.

It is believed, however, that the methods described in this bulletin will be of material assistance to chemists engaged in the analysis of the various types of blasting explosives.

APPENDIX.

TOLERANCES FOR PERMISSIBLE EXPLOSIVES.

At a conference on June 7, 1915, between manufacturers of explosives and the bureau's engineers and chemists an agreement was reached providing for reasonable limits of variation or "tolerances" in the results of analyses and tests of permissible explosives. If these tolerances are exceeded by a given lot of any permissible explosive it is not permissible. The tolerances established, which were made effective July 1, 1915, are stated as follows:

In order to define more exactly what is meant by the phrase "similar in all respects" in the definition of a permissible explosive, namely, "an explosive is called a permissible explosive when it is similar in all respects to the sample that passed certain

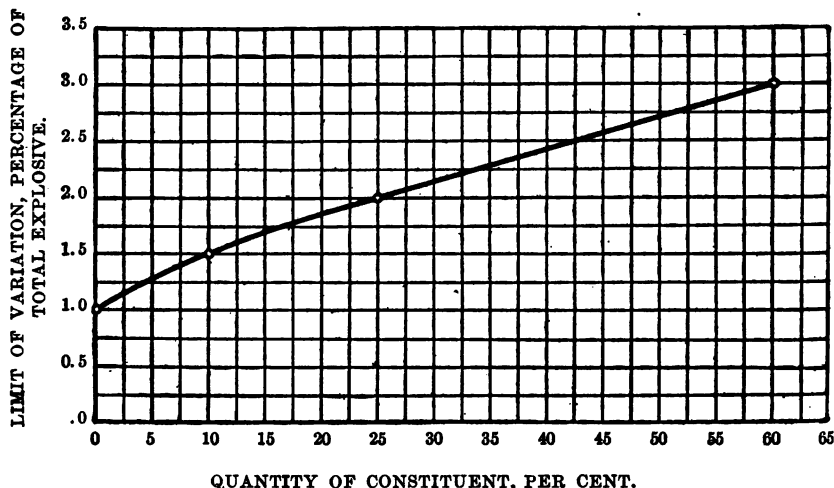


FIGURE 7.—Curve of limit variation in composition of permissible explosives.

tests by the United States Bureau of Mines, and when it is used in accordance with the conditions prescribed by this bureau," the following tolerances are recommended for field samples or manufacturers' samples of explosives, beyond which such lot of explosives can not vary and still be considered permissible for use in coal mines: *Provided*, That where the Bureau of Mines finds a sample which does not come up to the tolerance limits, the bureau shall simply declare that particular lot of explosives not permissible, and a copy of the notification to the consumer or owner shall be furnished the manufacturer, the notification to state that the explosive did not meet the tolerance requirements for moisture or ingredients, etc., as the case might be.

Chemical analysis.—Moisture, to be fixed by a sliding scale of from $1\frac{1}{2}$ per cent at zero to 4 per cent at 10 per cent of moisture in original sample, this tolerance being on total percentage of moisture in the explosive.

Other ingredients (or their equivalents) in quantities not exceeding 60 per cent, according to a curve [shown in figure 7]. For ingredients in quantities of 60 per cent

or more, the tolerance shall be plus or minus 3 per cent: *Provided*, That the ingredients of a permissible explosive shall be considered to be those substances reported as found by the Bureau of Mines in the original sample of that explosive submitted for test as to its permissibility: *And provided further*, That an equivalent shall be considered to be a substance which would not materially alter the properties of the explosive and which would produce the same result as the original substance.

Products of combustion (determined by Bichel gage test).—The volume of poisonous gases from 680 grams of the explosive, including its wrapper, must be less than 158 liters, except that in case the first test yields 158 liters or more of poisonous gases per 680 grams of the explosive, including its wrapper, the average result of three tests agreeing within 5 per cent of each other shall be taken, and no explosive shall remain permissible when this average for poisonous gases exceeds the above standard limit.

Physical tests.^a—

Rate of detonation (the average of three trials with Mettengang's recorder), plus or minus 15 per cent.

Unit defective charge (the average of three trials with the ballistic pendulum), plus or minus 10 per cent.

Grams of wrapper per 100 grams of explosive, plus or minus 2.0 grams (average of four determinations): *Provided*, That the manufacturers shall submit samples of all different sizes of cartridges, to be considered as part of the original sample, the amount of wrapper to be determined for each size of sample: *And provided further*, That the tolerances as suggested shall be determined in comparison with the various diameters of samples as submitted with the original sample.

Apparent specific gravity of cartridge, by sand, plus or minus 7.5 per cent (average of four determinations): *Provided*, that actual density shall be determined on cartridges of the same diameter as the standard: *And provided further*, That manufacturers shall be required to submit samples of all sizes.

Gas and dust gallery No. 1.—No ignition must be obtained in each of one or more trials. Note: In the retesting of permissible explosives by tests 1, 3, and 4,^b the charges of the explosives fired will be reduced 10 per cent in weight from the weights originally used in order to eliminate any likelihood of a failure being due to the natural variations in the gallery conditions.

Pendulum friction test.—Each explosive must pass a test of 10 trials under the same conditions as originally tested, except that the height of fall of the wood-fiber shoe will be reduced by 10 per cent in order to eliminate any likelihood of a failure being due to the natural variations in test conditions.

^a For methods of making these tests, see Hall, Clarence, and Howell, S. P., Tests of permissible explosives: Bull. 66, Bureau of Mines, 1913, 313 pp.

^b Op. cit., p. 303.

PUBLICATIONS ON MINE ACCIDENTS AND TESTS OF EXPLOSIVES.

A limited supply of the following publications of the Bureau of Mines is temporarily available for free distribution. Requests for all publications can not be granted, and applicants should select only those publications that are of especial interest to them. All requests for publications should be addressed to the Director, Bureau of Mines, Washington, D. C.

BULLETIN 15. Investigations of explosives used in coal mines, by Clarence Hall, W. O. Snelling, and S. P. Howell, with a chapter on the natural gas used at Pittsburgh, by G. A. Burrell, and an introduction by C. E. Munroe. 1912. 197 pp., 7 pls., 5 figs.

BULLETIN 17. A primer on explosives for coal miners, by C. E. Munroe and Clarence Hall. 61 pp., 10 pls., 12 figs. Reprint of United States Geological Survey Bulletin 423.

BULLETIN 20. The explosibility of coal dust, by G. S. Rice, with chapters by J. C. W. Frazier, Axel Larsen, Frank Haas, and Carl Scholz. 204 pp., 14 pls., 28 figs. Reprint of United States Geological Survey Bulletin 425.

BULLETIN 48. The selection of explosives used in engineering and mining operations, by Clarence Hall and S. P. Howell. 1913. 50 pp., 3 pls., 7 figs.

BULLETIN 51. The analysis of black powder and dynamite, by W. O. Snelling and C. G. Storm. 1913. 80 pp., 5 pls., 5 figs.

BULLETIN 56. First series of coal-dust explosion tests in the experimental mine, by G. S. Rice, L. M. Jones, J. K. Clement, and W. L. Egy. 1913. 115 pp., 12 pls., 28 figs.

BULLETIN 59. Investigations of detonators and electric detonators, by Clarence Hall and S. P. Howell. 1913. 73 pp., 7 pls., 5 figs.

BULLETIN 66. Tests of permissible explosives, by Clarence Hall and S. P. Howell. 1913. 313 pp., 1 pl., 6 figs.

BULLETIN 68. Electric switches for use in gaseous mines, by H. H. Clark and R. W. Crocker. 1913. 40 pp., 6 pls.

BULLETIN 69. Coal-mine accidents in the United States and foreign countries, compiled by F. W. Horton. 1913. 102 pp., 3 pls., 40 figs.

BULLETIN 72. Occurrence of explosive gases in coal mines, by N. H. Darton. 1915. 248 pp., 7 pls., 33 figs.

BULLETIN 80. A primer on explosives for metal miners and quarrymen, by C. E. Munroe and Clarence Hall. 1915. 122 pp., 15 pls., 7 figs.

TECHNICAL PAPER 6. The rate of burning of fuse as influenced by temperature and pressure, by W. O. Snelling and W. C. Cope. 1912. 28 pp.

TECHNICAL PAPER 7. Investigations of fuse and miners' squibs, by Clarence Hall and S. P. Howell. 1912. 19 pp.

TECHNICAL PAPER 11. The use of mice and birds for detecting carbon monoxide after mine fires and explosions, by G. A. Burrell. 1912. 15 pp.

TECHNICAL PAPER 12. The behavior of nitroglycerin when heated, by W. O. Snelling and C. G. Storm. 1912. 14 pp., 1 pl., 2 figs.

TECHNICAL PAPER 13. Gas analysis as an aid in fighting mine fires, by G. A. Burrell and F. M. Seibert. 1912. 16 pp., 1 fig.

TECHNICAL PAPER 17. The effect of stemming on the efficiency of explosives, by W. O. Snelling and Clarence Hall. 1912. 20 pp., 11 figs.

TECHNICAL PAPER 18. Magazines and thaw houses for explosives, by Clarence Hall and S. P. Howell. 1912. 34 pp., 1 pl., 5 figs.

TECHNICAL PAPER 21. The prevention of mine explosions, report and recommendations, by Victor Watteyne, Carl Meissner, and Arthur Desborough. 12 pp. Reprint of United States Geological Survey Bulletin 369.

TECHNICAL PAPER 30. Mine-accident prevention at Lake Superior iron mines, by D. E. Woodbridge. 1913. 38 pp., 9 figs.

TECHNICAL PAPER 39. The inflammable gases in mine air, by G. A. Burrell and F. M. Seibert. 1913. 24 pp., 2 figs.

TECHNICAL PAPER 44. Safety electric switches for mines, by H. H. Clark. 1913. 8 pp.

TECHNICAL PAPER 47. Portable electric mine lamps, by H. H. Clark. 1913. 13 pp.

TECHNICAL PAPER 48. Coal-mine accidents in the United States, 1896-1912, with monthly statistics for 1912, compiled by F. W. Horton. 1913. 74 pp., 10 figs.

TECHNICAL PAPER 61. Metal-mine accidents in the United States during the calendar year 1912, compiled by A. H. Fay. 1913. 76 pp., 1 fig.

TECHNICAL PAPER 62. Relative effects of carbon monoxide on small animals, by G. A. Burrell, F. M. Seibert, and I. W. Robertson. 1914. 23 pp.

TECHNICAL PAPER 67. Mine signboards, by Edwin Higgins and Edward Steidle. 1913. 15 pp., 1 pl., 4 figs.

TECHNICAL PAPER 71. Permissible explosives tested prior to January 1, 1914, by Clarence Hall. 1914. 12 pp.

TECHNICAL PAPER 77. Report of the Committee on Resuscitation from Mine Gases, by W. B. Cannon, G. W. Crile, Joseph Erlanger, Yandell Henderson, and S. J. Meltzer. 1914. 36 pp., 4 figs.

TECHNICAL PAPER 92. Quarry accidents in the United States during the calendar year 1913, compiled by A. H. Fay. 1914. 76 pp.

TECHNICAL PAPER 94. Metal-mine accidents in the United States during the calendar year 1913, compiled by A. H. Fay. 1914. 73 pp.

TECHNICAL PAPER 100. Permissible explosives tested prior to March 1, 1915, by S. P. Howell. 1915. 16 pp.

TECHNICAL PAPER 107. Production of explosives in the United States during the calendar year 1914, by A. H. Fay. 1915. 14 pp.

TECHNICAL PAPER 111. Safety in stone quarrying, by O. P. Bowles. 1915. 48 pp. 5 pls., 4 figs.

TECHNICAL PAPER 119. The limits of inflammability of mixtures of methane and air, by G. A. Burrell and G. G. Oberfell. 1915. 30 pp., 4 figs.

MINERS' CIRCULAR 5. Electrical accidents in mines, their causes and prevention, by H. H. Clark, W. D. Roberts, L. C. Ilsley, and H. F. Randolph. 1911. 10 pp., 3 pls.

MINERS' CIRCULAR 7. Use and misuse of explosives in coal mining, by J. J. Rutledge, with a preface by J. A. Holmes. 1913. 52 pp., 8 figs.

MINERS' CIRCULAR 8. First-aid instructions for miners, by M. W. Glasgow, W. A. Raudenbush, and C. O. Roberts. 1913. 67 pp., 51 figs.

MINERS' CIRCULAR 11. Accidents from mine cars and locomotives, by L. M. Jones. 1912. 16 pp.

MINERS' CIRCULAR 12. The use and care of miners' safety lamps, by J. W. Paul. 1913. 16 pp., 4 figs.

MINERS' CIRCULAR 13. Safety in tunneling, by D. W. Brunton and J. A. Davis. 1913. 19 pp.

MINERS' CIRCULAR 14. Gases found in coal mines, by G. A. Burrell and F. M. Seibert. 1914. 23 pp.

MINERS' CIRCULAR 15. Rules for mine-rescue and first-aid field contests, by J. W. Paul. 1913. 12 pp.

MINERS' CIRCULAR 16. Hints on coal-mine ventilation, by J. J. Rutledge. 1914. 22 pp.

MINERS' CIRCULAR 17. Accidents from falls of rock or ore, by Edwin Higgins. 1914. 15 pp., 8 figs.

MINERS' CIRCULAR 21. What a miner can do to prevent gas and dust explosions, by G. S. Rice. 1914. 24 pp.

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